ANALYTICAL ABSTRACTS

Dealing with all branches of Analytical Chemistry: Published Monthly with THE ANALYST by the Society for Analytical Chemistry

Editor: NORMAN EVERS, B.Sc., Ph.D., F.R.I.C.
14, BELGRAVE SQUARE, LONDON, S.W.1
Telephone: BELgravia 3258

Published for the Society by
W. HEFFER & SONS, LTD., CAMBRIDGE, ENGLAND

Volume 5 Price 8s.
Subscription Rate, inclusive of Index, 75s. per annum, Post Free
No. 12, Abstracts 3961-4412 December, 1958

FOR REVISED PRICES FROM 1st JANUARY, 1959, SEE OVERLEAF

Binding . . .

W. Heffer & Sons Ltd. announce that they are now able to BIND copies of ANALYTICAL ABSTRACTS, in an approved binding case, at a cost of 12/6 per volume. The 12 Parts for 1957 together with Index and remittance for 12/6 should be sent to

W. HEFFER & SONS, LIMITED
HILLS ROAD, CAMBRIDGE

IMPORTANT NOTICE TO SUBSCRIBERS

(Other than Members of the Society)

For 1959 the Subscription to *Analytical Abstracts*, inclusive of Index, will be £5 per annum; and for *Analytical Abstracts* together with *The Analyst* and Indexes will be £8 8s. per annum.

Analytical Abstracts is available printed on one side of the paper only, suitable for incorporation into reference systems; the cost will be £5 7s. 6d. per annum, exclusive of Index.

The price of single copies of *Analytical Abstracts*, including back numbers, will be 10s. 6d. post free.

All further enquiries about subscriptions should be made through the Secretary, the Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1. Telephone: BELgravia 3258.

now

available

WHATMAN

Glass

Fibre

Papers

- **excellent retention with rapid filtration**
- **high softening point**
- **outstanding chemical resistance**

These brilliant white, exceptionally strong papers are composed entirely of glass micro fibres with no added binding materials. Their excellent retention properties make them particularly useful for filtering very fine precipitates and semi-colloidal substances through a coarse porosity crucible. The filtration rate is very rapid, and there is no risk of blocking.

The papers are also recommended for routine filtration through Buchner and Hirsch funnels, and for certain applications in Chromatography and Electrophoresis. Although in the latter techniques they do not replace conventional Whatman papers, the intrinsic properties of Glass Fibre Papers can be utilised effectively for investigating non-aqueous systems, organic mixtures of protein origin and several other substances.

Please write for technical literature.

H. REEVE ANGEL & CO LTD
9 BRIDEWELL PLACE LONDON EC4
also at 52 DUANE STREET NEW YORK 7
sole distributors of
WHATMAN FILTER PAPERS
(manufacturers W. & R. Whatman Ltd.)

Binding . . .

W. Heffer & Sons Ltd. announce that they are now able to BIND copies of ANALYTICAL ABSTRACTS, in an approved binding case, at a cost of 12/6 per volume. The 12 Parts for 1957 together with Index and remittance for 12/6 should be sent to

W. HEFFER & SONS, LIMITED
HILLS ROAD, CAMBRIDGE

IMPORTANT NOTICE TO SUBSCRIBERS

(Other than Members of the Society)

For 1959 the Subscription to *Analytical Abstracts*, inclusive of Index, will be £5 per annum; and for *Analytical Abstracts* together with *The Analyst* and Indexes will be £8 8s. per annum.

Analytical Abstracts is available printed on one side of the paper only, suitable for incorporation into reference systems; the cost will be £5 7s. 6d. per annum, exclusive of Index.

The price of single copies of *Analytical Abstracts*, including back numbers, will be 10s. 6d. post free.

All further enquiries about subscriptions should be made through the Secretary, the Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1. Telephone: BELgravia 3258.

now

available

WHATMAN

Glass

Fibre

Papers

- **excellent retention with rapid filtration**
- **high softening point**
- **outstanding chemical resistance**

These brilliant white, exceptionally strong papers are composed entirely of glass micro fibres with no added binding materials. Their excellent retention properties make them particularly useful for filtering very fine precipitates and semi-colloidal substances through a coarse porosity crucible. The filtration rate is very rapid, and there is no risk of blocking.

The papers are also recommended for routine filtration through Buchner and Hirsch funnels, and for certain applications in Chromatography and Electrophoresis. Although in the latter techniques they do not replace conventional Whatman papers, the intrinsic properties of Glass Fibre Papers can be utilised effectively for investigating non-aqueous systems, organic mixtures of protein origin and several other substances.

Please write for technical literature.

H. REEVE ANGEL & CO LTD

9 BRIDEWELL PLACE LONDON EC4

also at **52 DUANE STREET NEW YORK 7**

sole distributors of

WHATMAN FILTER PAPERS

(manufacturers W. & R. Balston Ltd)

organic chemical reagents

Hopkin and Williams Ltd. have been noted, for many years, for their range of Organic Reagents for the detection or determination of metals, and other radicals, and the Company is publishing, regularly, a series of Monographs relating to these reagents.

The following Monographs are available free on request:—

No. 34 CARMINE—Reagent for Boron.

No. 35 2:4-XYLENOL—Reagent for Nitrate.

No. 36 *p*-BROMOMANDELIC ACID—Reagent for Zirconium.

Previous Monographs in the series have already been issued in collective form, under the title "Organic Reagents for Metals, and Other Reagent Monographs", Volume 1. Copies of this publication are still available at 15/- nett, post free, and full details will be sent on request.

HOPKIN & WILLIAMS Limited

CHADWELL HEATH · ESSEX · ENGLAND

Branches in LONDON · MANCHESTER · GLASGOW · Agents throughout the U.K. and all over the world.

ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

3961. **The importance of buffered solutions in analytical chemistry.** P. Zuman (Polarographic Inst., Acad. Sci., Prague). *Chemie, Prague*, 1957, **9** (2), 172–183.—An informative discussion of practical importance. J. ZÝKA

3962. **Modifications in the analytical scheme for the hydrochloric acid group.** M. Carranza Márquez. *Bol. Soc. Quím. Peru*, 1957, **23**, 1–5.—The chlorides of Tl and Pb are separated by the use of pyridinium bismuth iodide in acetone. *Preparation of reagent*—To pyridine (20 g) add dil. HNO_3 (1:2) (20 ml), cool, add H_2O (30 ml) followed by KI soln. (10%) and then $Bi(NO_3)_3$ soln. (10%). Filter off the ppt., dry in the air and dissolve in acetone. *Procedure*—To the sample soln. add 6 *N* HCl, and wash the ppt. obtained (containing the chlorides of Ag, Hg, Pb and Tl and H_2WO_4) with boiling water to dissolve TlCl and $PbCl_2$. To this soln. add dil. HNO_3 followed by pyridinium bismuth iodide reagent and acetone. Shake and filter off the reddish-yellow Tl complex, which can be dissolved in KBr_3 for further confirmation tests. To the filtrate containing the soluble Pb complex add NaOH soln. (20%) and heat to decompose the complex. Filter off the bismuth hydroxide, acidify with acetic acid and add K_2CrO_4 soln. (5%) to precipitate $PbCrO_4$. The ppt. containing the chlorides of Hg and Ag, and H_2WO_4 (see above) is washed with NaOH (2 *N*) and the Na_2WO_4 soln. formed is treated with Zn and H_2SO_4 to produce a blue colour. The residue of AgCl, HgO and Hg left after washing the ppt. with NaOH soln. is treated with aq. NH_3 soln., and Ag and Hg are detected in the usual way. G. H. FOXLEY

3963. **The use of evaporation analysis for the detection of minute traces of material. I. Experimental technique.** W. Geilmann (Univ. Mainz, Germany). *Z. anal. Chem.*, 1958, **160** (6), 410–426.—The apparatus comprises a quartz tube with an inlet for the carrier gas, a section to contain a boat for the sample, and a fused-in jet to direct the gas stream on to the end surface of a cold finger. If the determination is to be made spectrographically, the cold finger is made of metal and capped with metal foil to serve also as the spectrographic electrode. The apparatus must be accurately constructed. The tube is heated to within $\pm 10°$ of any desired temp. up to 1200° by a cylindrical heater. The method is applicable to any material which evaporates and condenses under these conditions provided that it is not mixed with other volatile material. Traces can be pptd. from very dil. soln. with a carrier from which they can be volatilised. The carrier gas may be inert or reactive to yield volatile compounds. As large samples may be treated without the addition of large quantities of reagents and the consequent risk of introducing contamination, amounts of the order of 10^{-9} g in 0·5 litre of soln. can be estimated. G. BURGER

3964. **New principle in semi-quantitative spot analysis.** M. P. Polyakov and V. P. Polyakova. *Byull. Nauch.-Tekh. Inform. Arm. Nauch. Inst., Zemled.*, 1957, (2), 32–36; *Ref. Zhur., Khim.*, 1958, Abstr. No. 21,082.—A drop analysis method for visual estimation is proposed, based on the titration, with the soln. to be analysed, of paper steeped in an indicator and the standard soln. A standard soln. of Ag^+ is used for the determination of chlorides, and of Ba^{2+} for sulphates. The soln. being analysed is transferred to the centre of the spot in as small portions as possible, each fresh portion being added only after the previous portion has soaked into the paper. The end-point is shown by the change of colour of the indicator. When determining chlorides, K_2CrO_4 is used as indicator. The concn. of substance is determined empirically from the size of the spot, the comparison with a scale being made after the moist spot has ceased to spread. The method of determining Cl^- and a suitable apparatus are described. C. D. KOPKIN

3965. **Analytical use of tetraphenylborates.** A. Heyrovský (II. Intern. Hospital, Charles' Univ., Prague). *Chemie, Prague*, 1957, **9** (1), 100–103.—A review, with 50 references. J. ZÝKA

3966. **Importance of ascorbic acid in analytical chemistry.** H. Tůma and V. Šanda (Res. Inst. Materials and Technol., Prague). *Chemie, Prague*, 1957, **9** (3), 390–394.—A survey of colorimetric and volumetric methods in which ascorbic acid is used as reducing agent. (21 references.) J. ZÝKA

3967. **Analysis for industry.** [**Complexones.** [**I; II**]. T. S. West. *Ind. Chem. Mfr*, 1958, **34**, 37–39; 89–91.—Analytical applications of some of the less common complexones are reviewed and discussed. (27 references.) S.C.I. ABSTR.

3968. **Reference standards for EDTA solutions.** P. F. Lott and K. L. Cheng (Engng Dept., Univ. of Missouri School of Mines & Metall., Rolla, U.S.A.). *Chemist Analyst*, 1958, **47** (1), 8–9.—It is suggested that magnesium acetate tetrahydrate (**I**), dried overnight in a desiccator over $CaCl_2$, and zinc ammonium sulphate hexahydrate (**II**) are suitable standards for the titration of EDTA soln. **II** is more hygroscopic than **I**, but has a higher equiv. wt. Magnesium sulphate heptahydrate, dried overnight over $CaCl_2$, or preferably over a mixture of its hydrates, is also suitable. R. E. ESSERY

3969. **Catechol violet.** V. Suk and M. Malát (Inst. Anal. Chem., Charles' Univ., Prague). *Chemie, Prague*, 1957, **9** (2), 195–209.—The properties, reaction mechanism and practical use of this

complexometric indicator are reviewed. The direct titration of Bi, Th, Cu, Fe, Ga, In, Ni, Co, Mn, Zn, Mg and Cd, and some indirect determinations, as well as possibilities of the use of catechol violet in qualitative analysis and in colorimetry, are described. (53 references.) J. ZÝKA

3970. **Further oo′-dihydroxyazo indicator dyes for EDTA titrations. [II].** R. Belcher, R. A. Close and T. S. West (Dept. of Chem., Univ. of Birmingham, England). *Chemist Analyst*, 1958, **47** (1), 2–4.—A report is presented on the properties of 13 dyes, giving name, constitution, working pH, colour change, sharpness, and whether the titration proceeds best in hot soln., with reference to the determination of Ca, Sr, Mg, Mn, Fe, Cd, Ni, Cu, Zn, In and Th. Some of these indicators show little advantage over established indicators, but others offer definite advantages for the determination of one or more of the metals mentioned, and these are critically compared with established indicators. The indicator possibilities of the remaining dyes are discussed. (*Cf. Anal. Abstr.*, 1958, **5**, 2497.)
R. E. ESSERY

3971. **Recent oxidation - reduction volumetric reagents. I. Titrations with potassium periodate.** A. Berka (Inst. Anal. Chem., Charles' Univ., Prague). *Chemie, Prague*, 1958, **10** (1), 40–44.—Volumetric determinations of inorganic compounds with KIO_4 are reviewed. (17 references.)

II. Titrations with potassium ferricyanide. A. Berka and J. Vulterin. *Ibid.*, 1958, **10** (2), 113–120.—A survey, with 29 references.

III. Titration with chloramine T. A. Berka. *Ibid.*, 1958, **10** (2), 121–129.—A survey, with 45 references. J. ZÝKA

3972. **Urea solutions as titration media and the basicity of urea.** M. Levy. *Compt. Rend. Lab. Carlsberg, Sér. Chim.*, 1958, **30** (16), 291–300 (in English).—Results are given for the titration of soln. of urea with *N* HCl and *N* KOH. Titrant was added from a micrometer syringe to 10 ml of soln., with mechanical stirring and exclusion of CO_2 by means of a stream of N, and the pH measured at 20° ± 0·02° with glass and satd. calomel electrodes. It is shown that urea is a weak base, and that its titration constant depends on its concentration, the line of best fit, on certain assumptions, being given by $pK'_u = 0{\cdot}22 - 2{\cdot}3 \log (H_2O)$. The addition of KOH to urea soln. increases the observed pH over that shown by water alone, so that urea is not a proton donor. A discussion is given, based on the Brønsted acid - base theory, and the data are explained by the difference in hydration between reactants and products in proton donor - acceptor reactions. This hypothesis gives calculated pK values for the titration of acetic acid in urea soln. which are in good agreement with those observed. R. E. ESSERY

3973. **Titrations in the presence of chemiluminescent indicators.** L. Erdey (Budapest Univ.). *Magyar Kém. Lapja*, 1958, **13** (1), 7–12.—Theory and applications are reviewed. Lucigenin (5:5′-diacridyl dimethonitrate) (**I**) is used as acid - base indicator for the determination of acidity of turbid or coloured solutions such as milk, molasses, fruit juices and mustard and for titration of salicylic and acetylsalicylic acids. The acid value of plant oils and fats is determined in amyl alcohol soln. (30 ml) by adding 1 or 2 drops of a 30% soln. of H_2O_2 and 1 drop of 0·5% soln. of **I**, and titrating with 0·5 *N* ethanolic KOH. As **I** is sensitive only to H_2O_2 and no other oxidant, Cr^{III} can be determined by oxidising it with known alkali hypobromite soln. and titrating the excess with H_2O_2. The accuracy is within − 0·08 to + 0·7%. Luminol (3-aminophthalhydrazide) is employed as redox indicator in micro-analysis, 0·001 *N* NaOBr being used. Lophine (2:4:5-triphenyliminazole) can be applied to the determination of several inorganic acids.
G. SZABO

3974. **Observations on the permanganate - arsenous oxide titration.** A. V. DeThomas and W. C. Purdy (Univ. of Connecticut, Storrs, U.S.A.). *Anal. Chim. Acta*, 1958, **18** (3), 185–188.—The reduction of MnO_4^- with As_2O_3 in dil. $HClO_4$ or 0·1 *M* H_2SO_4 produces a green soln. of an unstable manganic arsenate complex. In more concentrated H_2SO_4 an unstable pink manganic sulphate complex is formed. The sulphate complex is also formed when $MnSO_4$ is oxidised with PbO_2 in dil. H_2SO_4 or dil. $HClO_4$. The polarographic behaviour of both complexes is described. W. C. JOHNSON

3975. **End-point determination by interpolation in potentiometric micro-analysis.** F. L. Hahn (Angel Urraza 718–303, Mexico 12, D.F., Mexico). *Mikrochim. Acta*, 1958, (3), 395–401.—It is shown that the method given by Kolthoff for interpolation of end-points (the null value of the second differential being taken as the end-point) gives inaccurate results since it is based on the false assumption that the end-point always occurs at the mid-point of the measured portion. Simple interpolation procedures that give exact end-points are described and examples are given. S. M. MARSH

3976. **Quantitative methods of gas chromatography.** H. H. Hausdorff (Perkin Elmer A.-G., Scheuchzerstr. 7, Zurich, Switzerland). *Chemikerztg.* 1957, **81** (12), 392–396.—A review.
E. G. CUMMINS

3977. **New trends in gas chromatography.** J. Janák (Ústav Pro Naftový Výzkum, Brno, Czechoslovakia). *Chemie, Prague*, 1957, **9** (1), 20–24.—Problems connected with suitable fillings for chromatographic columns and the detection of separated compounds are discussed. J. ZÝKA

3978. **Use of ion exchangers in inorganic analysis.** L. Wünsch (Res. Inst. Inorg. Chem. Ústí nad Labem, Czechoslovakia). *Chemie, Prague*, 1957, **9** (1), 24–34.—A review is presented, with some practical examples. (30 references.) J. ZÝKA

3979. **Errors in colorimetry.** L. Novotný (Inst. Phys. Chem. and Anal. Chem., High School of Chem. Technol., Prague). *Chemie, Prague*, 1957, **9** (3), 324–345.—Sources of errors in colorimetry and their mathematical evaluation are discussed.
J. ZÝKA

3980. **Luminescence in analytical chemistry.** Z. Holzbecher (Inst. Anal. Chem., High School Chem. Technol., Prague). *Chemie, Prague*, 1958, **10** (1), 35–39.—A survey of the principles of luminescence and its use in analysis. J. ZÝKA

3981. **Use of catechol in photometric analysis.** V. Patrovský (Central Geolog. Inst., Prague). *Chemie, Prague*, 1958, **10** (2), 93–96.—Photometric determinations of Ti, Mo, V, W, Nb, Ta, U and Ce with catechol in various materials are reviewed.
J. ZÝKA

3982. **Use of oscillopolarographic methods in chemical analysis.** J. Doležal (Inst. Anal. Chem., Charles' Univ., Prague). *Chemie, Prague*, 1957, **9** (2), 184–195.—A review, with figures and 60 references. J. ZÝKA

3983. **Activation analysis.** P. Schiller (Inst. Anal. Chem., High School Chem. Technol., Bratislava, Czechoslovakia). *Chemie, Prague*, 1958, **10** (1), 26–35.—A review, with practical examples. (14 references.) J. ZÝKA

3984. **Radio-isotopes in analytical chemistry.** R. Jirkovský (Vysoká Škola Báňská, Ostrava, Czechoslovakia). *Chemie, Prague*, 1957, **9** (3), 345–366.—A review, with 45 references. J. ZÝKA

3985. **Analysis by isotopic dilution.** J. Tölgyessy (Inst. Anal. Chem., High School of Chem. Technol., Bratislava, Czechoslovakia). *Chemie, Prague*, 1958, **10** (2), 100–104.—A survey, with 32 references. J. ZÝKA

See also Abstracts—**3988**, Tolylarsonic acids as reagents. **4001**, Diphenyldi-*o*-tolyloxamidine as reagent. **4011**, Beryllon II as indicator for complexometric titrations. **4089**, Use of 4-amino-4′-chlorodiphenyl for W^{VI} and Mo^{VI}. **4144**, Use of ammonium *p*-aminophenyldithiocarbamate for Rh and Ir. **4145**, Use of 5-aminothiazoline-2-thiocarboxyamide. **4246**, Bis-(*p*-dimethylaminophenyl)amine as reagent for fatty acids.

2.—INORGANIC ANALYSIS

3986. **Chelometric titrations using an azoarsonic acid indicator.** J. S. Fritz, R. T. Oliver and D. J. Pietrzyk (Inst. for Atomic Res., Iowa State Coll., Ames, U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1111–1114.—Arsenazo forms red-violet complexes with many metals in acid or basic soln. and can be used in a colour test for the rare earths (*cf.* Kuznetsov, *Brit. Abstr. C*, 1953, 108). The rare earths and Y can be titrated directly with 0·05 *M* EDTA (disodium salt) at pH 5 to 6·5, with two drops of a 0·5% aq. soln. of arsenazo as indicator, or between pH 5 and 10 when interfering metal ions are present. Aluminium is masked as sulphosalicylate, small amounts of U, Fe, Co, Ni, Cu, Zn, Cd, Ag, Hg or Pb are masked by addition of 0·5 *M* diethyldithiocarbamate soln., but larger amounts of any of these metals should be removed by extraction of their diethyldithiocarbamate complexes pptd. at pH 5·5 to 7·0. If Ca or Mg or both are present the titration is made at pH 5·5. Thorium interferes with the titration of rare earths, but can be titrated at pH 1·7 to 3·0 even in the presence of U and moderate amounts of SO_4^{2-}, sulphosalicylate, catechol or carboxylic acids. The precision and accuracy of the various arsenazo-indicator procedures given are excellent. A comparison is made between the utility of this indicator and that of SPADNS (1:8-dihydroxy-2-*p*-sulphophenylazonaphthalene-3:6-disulphonic acid). W. J. BAKER

3987. **Electro-chromatography in the separation of ions. IV. Separation of copper- and tin-group metals.** Anil Kumar Majumdar and B. R. Singh (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1958, **18** (3), 220–223.—A technique previously described (*cf. Anal. Chim. Acta*, 1956, **15**, 547; 1957, **17**, 228, 541) is applied to the copper and tin groups of metals. The migration sequences are investigated in several electrolytes, some of them complex-forming substances. A soln. of 0·1 *N* KCl is most effective with Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+} and Cd^{2+}, all five ions being separated in 5 hr. with a potential of 150 V. Separations of binary mixtures only are achieved in the group comprising As^{3+}, Sb^{3+} and Sn^{2+}.

V. Separation of third-group metals. Anil Kumar Majumdar and B. R. Singh. *Ibid.*, 1958, **18** (3), 224–225.—The migration sequences of Be^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Ti^{4+}, Zr^{4+}, Th^{4+} and UO_2^{2+} are determined in various electrolytes. Separations are possible with some mixtures containing up to four constituents. W. C. JOHNSON

3988. **Metal precipitation with tolylarsonic acids.** A. Musil and R. Pietsch (Inst. f. anorg. u. anal. Chem., Univ., Graz, Austria). *Mikrochim. Acta*, 1957, (6), 796–802.—The differences of *o*-, *m*-, and *p*-tolylarsonic acids in their precipitating behaviour are discussed and compared with those of other acids. D. F. PHILLIPS

3989. **Analysis of hard metal and cutting metal.** C. Streil. *Chem. Tech., Berlin*, 1957, **9** (11), 672–675.—Methods are given for the determination of sp. gr., total C, graphite, and metal content of the carbides of W, Ti, Mo, Cr and V in hard metal. Total C is determined by a combustion analysis usual for steel. For the graphite content, 2 to 3 g of the sample is heated with 50 ml of 50% HCl with the subsequent addition of 15 ml of HF; the graphite is filtered on an asbestos pad and ignited, and the CO_2 is collected and measured. Hard metals based on tungsten carbide are analysed by dissolution in HCl-HF, pptn. of tungstic acid and ignition to the oxide. Titanium, Fe, Co and Ni are determined in the filtrate by usual methods. Titanium carbide-based materials are analysed for secondary constituents (Ni, Cr, V, Fe, Co and W), and for TiC by difference, after being heated to 1000° for conversion into oxides, fused with $KHSO_4$ and dissolved in aq. HCl. J. L. PROSSER

3990. **Rapid and simple method for the analysis of anti-friction metals.** M. E. Garate and M. T. Garate (Lab. Central de la R.E.N.F.E., Madrid, Spain). *Chim. Anal.*, 1958, **40** (3), 77–79.—The alloy is dissolved in a mixture of equal vol. of water, conc. HNO_3 (*d*, 1·33) and HF (*d*, 1·113) on a hot-plate at 100° to 110°, boiled to remove nitrous fumes, cooled, and diluted to 1 litre. The soln. remains clear, and the metals are determined in separate aliquots without the necessity for removing metals other than the one being determined. Dissolution is rapid (10 min. for 10 g of lead-base alloy at 80° to 100°, and 5 min. for tin-base alloy at room temp.), and the soln. remains clear on dilution, as the complex SnF_6^{2-} and SbF_6^- are stable and do not hydrolyse on dilution. The specified concn. of HNO_3 must be used; if HNO_3 (*d*, 1·38) is employed, the attack is incomplete. Lead is determined as $PbSO_4$; Cu (in concn. < 2%) colorimetrically with Na diethyldithiocarbamate, and in concn. > 2% electrolytically; Sb is reduced with SO_2 and titrated with $KBrO_3$, with methyl orange as indicator; Sn, after destruction of the SnF_6^{2-} and reduction to the stannous state with urea and metallic aluminium, is titrated with $KBrO_3$, with starch-iodide as indicator. Full manipulative details are given for each estimation. R. E. ESSERY

3991. **Quantitative spectrochemical determination of impurities in binary brasses.** L. N. Filimonov and A. I. Essen. *Trudy Gos. Nauch. i Proektn. Inst. po Obrabotke Tsvetn. Met.*, 1957, (16), 127–148; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,615.—To increase the sensitivity of the analysis, excite the spectrum by the action of a d.c. arc at 5·8 amp. on a small amount of sample converted into oxides by dissolving in HNO_3 and igniting. Grind the oxides and press into tablets of 6 mm diam. under a total pressure of 1500 kg. Prepare standards from Cu, Zn, Fe, Pb, Bi, As_2O_3, Sb_2O_3 and SnO_2, treat as described above, and press into tablets. Place the upper copper electrode and the lower graphite electrode (diam. 10 mm, with a cavity) in water-cooled clamps. First make the sample the cathode and melt it in the arc for 120 sec.; spectra are then obtained with an exposure of 80 sec. for the determination of Fe, Pb and Sn. Then reverse the polarity and, with an ignition time and exposure of 60 sec. each, spectra are obtained for As, Bi and Sn. Construct calibration curves with the lines (in A) Fe 2936·905, Pb 2873·3, Bi 2897·9, Sb 2598·06, As 2349·8 and Sn 2839·9. The concn. which can be determined vary from 0·001 or 0·005 to 0·03 or 0·20%. Special tests have shown that when the spectra are excited not from the oxide melt but by using a mass of metal as an electrode, the sensitivity of the determinations decreases and falls outside the accepted limits. The influence of Si and Sn on the accuracy of the analysis is studied. The coeff. of variation of the determination is $\simeq 15\%$.

C. D. KOPKIN

3992. **Analysis of mixtures of ortho- and para-hydrogen and the catalytic conversion orthohydrogen $\rightleftarrows$ parahydrogen.** F. Botter and G. Dirian (Centre Études Nucleaires, Saclay, France). *Comm. Énergie Atomique, France*, Rappt. No. 589, 1956, 25 pp.—Properties of and methods for the determination of ortho- and para-hydrogen are reviewed. A continuously recording apparatus developed for the analysis of mixtures is based on a bridge for measurement of thermal conditions, there being a difference of about 5% at room temp. The error in the method ranges from 0·2% for a mixture containing 25 mole % para-hydrogen to $\pm$ 1% for an equimolecular mixture. Several absorbants are assessed for catalytic activity at $-$ 195° for the heterogeneous conversion ortho-hydrogen $\rightleftarrows$ para-hydrogen. Activated carbon is least active; a Cr_2O_3 - Al_2O_3 catalyst is highly active. Paramagnetic conversion is first order. (49 references.)

CHEM. ABSTR.

3993. **Micro-determination of deuterium by effusiometry.** D. A. Lee (Chem. Div., Oak Ridge National Lab., Tenn.). *Anal. Chem.*, 1958, **30** (7), 1296–1298.—Compounds containing D are converted into H - D gas by causing them to react with uranium metal turnings at 500°, and the rate of effusion of the gas through an orifice is measured with a matched pair of thermistors as a pressure gauge. Deuterium can be determined to within $\pm$ 1%. The determination can be carried out with very small quantities (0·1 ml) of gas under standard conditions.

K. A. PROCTOR

3994. **Determination of catalyst water by exchange with deuterium gas.** J. K. Lee and S. W. Weller (Houdry Process Corp., Linwood, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1057–1058.—The amount of H_2O (or equiv. OH) in oxide catalysts can be determined by isotopic exchange of H with gaseous D at 300° to 500° in a high-vacuum system with an all-glass circulating pump to re-cycle the gas in a closed system. After 16 hr. the isotopic composition of the gas is determined by mass spectrometry, and from this and the amount of D initially introduced the percentage of H_2O can be calculated. The method is non-destructive for refractory oxides, and non-volatile components do not interfere. The accuracy is as high as that of the ignition-loss method.

W. J. BAKER

3995. **Sampling and analysis for impurities in liquid sodium systems.** J. R. Humphreys, jun. (Argonne Nat. Lab., Lemont, Ill.). *Chem. Eng. Progr. Symposium Ser.*, **53**, No. 20, 1957, 7–10.—The sampler developed at Argonne National Lab. is described. A representative sodium sample is drawn into a metal-foil-lined metal receiver. The sodium is removed from its non-volatile impurities directly in the sampler by vacuum-distillation, and the residue is then analysed by standard radiological or chemical methods. This method of sampling and of impurity separation is also applicable to other liquid-metal systems such as K, Na - K alloys, Hg, Rb and Cs. The sampler is easily adaptable to remote-controlled operation for use with radioactive systems.

CHEM. ABSTR.

3996. **Rapid method of control of metallic potassium for the content of potassium and sodium.** Z. S. Bannŷkh and A. P. Sachko. *Trudŷ Ural'sk. Nauch. Khim. Inst.*, 1957, (4), 209–217; *Ref. Zhur., Khim.*, 1958, Abstr. No. 24,880.—A rapid method is described for the determination of Na in metallic potassium by measurement of the solidification temp. The dependence of the solidification temp. on the content of Na is established. Place 70 to 80 g of sample in a tube in an oil bath heated to about 100° and slowly heat. After the metal has melted insert a thermometer (0° to 100° with divisions in 0·1° or 0·2°) protected at the lower end with an iron cap of thickness 0·1 to 0·2 mm, cover the molten metal with a layer of Vaseline, and heat to 75° or 80°. Remove the oil bath, cool the tube in the air and note the commencing and final solidification-point. The content of Na is found from a calibration curve constructed in analogous fashion from alloys with known content of Na. The abs. error of the method is 0·1 to 0·2%. To determine total Na plus K, place 2 to 2·5 g of metal in a N-filled solution apparatus consisting of a round-bottomed flask in a bath of cooled 96% ethanol, fitted with a coil-pipe and dropping funnel. Pass N through the apparatus for 2 or 3 min. and add 96% ethanol dropwise with shaking. When solution is complete, make the contents of the flask up to 200 ml, and titrate a 20-ml aliquot with 0·25 *N* HCl to methyl orange. The content of K is found by difference. The abs. error of the determination of K is $\simeq 0{\cdot}5\%$.

C. D. KOPKIN

3997. **Analytical determination of radio-caesium as tungstophosphate.** V. I. Spitsŷn and N. B. Mikheeva. *Atomn. Energiya*, 1957, **3** (9), 255–256; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,537.—This radiometric determination of Cs consists in pptng. Cs as caesium tungstophosphate (**I**), dissolving the ppt. in a known vol. of alkali and measuring the activity of the soln. The solubility of **I** is 0·0034 millimole per litre. To 1 ml of the soln. to be analysed, containing uranium disintegration products (the content of U should be $\geq$ 0·1 g per litre), in a 10-ml centrifuge tube, add

0·5 to 1 ml of conc. HNO_3 and 1 ml of CsCl (7 g per litre) or $CsNO_3$ soln., mix, heat on a water bath, and add 1 ml of sodium tungstophosphate soln. [5·5 g of $Na_3H_4[P(W_2O_7)_6].19H_2O$ in 100 ml of 5% HNO_3]. Warm for 10 min. on the water bath, cool, centrifuge and wash the ppt. three times with 10% HNO_3 (5 to 10 ml). Re-precipitate the washed residue twice, by dissolving it in 1 ml of 15% NaOH soln., adding 2 to 5 mg of $NaH_2PO_4.H_2O$, conc. HNO_3, dropwise, and 0·5 ml of sodium tungstophosphate soln., warming for 10 min. on a water bath, cooling and centrifuging. Dissolve the ppt. in 1 ml of 15% KOH soln., add to the soln. 5 or 10 ml of water and 1 ml of a 0·1% $Fe(NO_3)_3$ soln. [the $Fe(OH)_3$ formed carries traces of other radioisotopes into the ppt.], shake, and make up to a known vol. Remove the $Fe(OH)_3$ ppt. before measuring the activity of the soln. Rubidium is determined together with Cs. The presence of Na, Mg, alkaline-earth metals, Al, K (< 10 g per litre), Cl^-, NO_3^-, SO_4^{2-} or acetate does not cause interference. C. D. KOPKIN

3998. **Micro-determination of copper.** W. N. Ghelberg and M. Gagiu (Med.-Pharm. Inst., Cluj, Romania). *Rev. Chim., Bucharest*, 1958, **9** (2), 99–100.—This colorimetric method is based on the use of tetrahydrostrychnine, and can be used between limits of 0·00001 and 1·00 mg of Cu per ml with a sensitivity between 1 in 10^{-8} and 1 in 10^{-4} mg of Cu per ml. It is not applicable in the presence of Mn^{7+}, Cr^{3+} or Cr^{6+}, or of small amounts of Fe^{3+}, Mg^{2+}, NO_2^-, PO_4^{3-} or $[Fe(CN)_6]^{3-}$. H. SHER

3999. **New semi-micro gravimetric method for the determination of copper.** V. Armeanu and D. Bardan (Polytech. Inst. of Bucharest). *Rev. Chim., Bucharest*, 1958, **9** (2), 105–106.—The method is based on the formation of a ppt. by the interaction of copper salts with *m*-phenylenediamine (**I**) and mercuric potassium iodide (**II**). *Procedure*—A soln. containing 0·05 g to 0·2 g of $CuSO_4.5H_2O$ in 10 to 20 ml is slightly acidified with H_2SO_4, and 4 to 5 ml of 10% Na acetate soln. is added, followed by a slight excess of **I** until a black colour is produced. The ppt. is dissolved in dil. H_2SO_4, care being taken that the pH does not fall below 2. To this soln. is added drop by drop a soln. of **II**, until the pptn. of the black crystals is complete. The mixture is then well agitated and allowed to settle for 15 min. The ppt. is filtered off, washed 3 or 4 times with 5 ml of washing soln. [1 ml of $HgCl_2$ soln., containing the minimum of KI to maintain the soln., diluted to 100 ml, plus 1 ml of **I** soln. (2%) diluted with 20 ml of water], then twice with 2 to 5 ml of water, and dried at 105° to 110°. H. SHER

4000. **2:2′-Diquinolyl and its use in the photometric determination of copper in metals and alloys.** A. L. Gershuns. *Trudy Nauch.-Tekh. Ob. Chernoĭ Metallurg., Ukr. Resp. Pravl.*, 1956, **4**, 149–153; *Ref. Zhur., Khim.*, 1958, Abstr. No. 28,404.—2:2′-Diquinolyl (**I**) is used for the determination of Cu in the analysis of metallic aluminium, zinc, magnesium and silumin. Tartaric acid at pH 5 to 6 is used to keep Zn or Al in soln. during the determination of small amounts of Cu. To obtain satisfactory results with a single extraction of Cu with a 0·02% soln. of **I** in *iso*amyl alcohol, intensive mixing of the soln. is essential in a thermostat controlled to within 1° or 2°. The extinction is measured at 545 mμ. The method may be used for the determination of 0·01 to 0·1% of Cu. C. D. KOPKIN

4001. **Colorimetric method for the determination of copper with diphenyldi-o-tolyloxamidine.** E. Papafil, M. Papafil, A. Kleinstein and V. Macovei (Univ. "Al. I. Cuza," Iaşi, Romania). *An. Ştiinţ. Univ. "Al. I. Cuza" din Iaşi, Sect. I*, 1956, **2** (1–2), 241–250.—The yellow colour obtained by the reaction between the reagent and copper salts can be measured for amounts down to 0·25 μg per ml. The intensity varies with the concn., according to the Beer - Lambert law. It is claimed that the method is simple, rapid and exact. H. SHER

4002. **Composition of cupric o-cresotate [2-hydroxy-*m*-toluate] chelates: a colorimetric study.** S. C. Tripathi and Satya Prakash (Chem. Lab., Univ. of Allahabad). *J. Indian Chem. Soc.*, 1958, **35** (2), 139–143.—In 1:1 mixtures of $CuSO_4$ and sodium 2-hydroxy-*m*-toluate, the green colour becomes more intense with increase in pH, the max. colour being produced at pH 5·2. The composition of the complex at pH 5·2 and 5·0 is found to be Cu^{2+} and 2-hydroxy-*m*-toluate in a 1:1 ratio. In 1:2 and 1:3 mixtures of $CuSO_4$ and sodium 2-hydroxy-*m*-toluate, the colorimeter readings show a max. at pH 5·7. The composition of this complex is found to be Cu^{2+} and 2-hydroxy-*m*-toluate in a 1:2 ratio. Intermediate mixtures of the two complexes exist between pH 5·7 and 5·2. I. JONES

4003. **Polarographic studies in a basal solution of fused borax. I. The polarography of copper and cadmium.** Yu. K. Delimarskiĭ and K. M. Kalabalina. *Ukr. Khim. Zhur.*, 1957, **23** (5), 584–592; *Ref. Zhur., Khim.*, 1958, Abstr. No. 24,724.—Fused borax at 840° is reduced at a stationary platinum cathode of length 0·25 mm at a potential of 1·34 V with reference to a platinum anode of surface 2·5 sq. cm. In a basal soln. of fused borax, CuO and CdO form distinct waves, the heights of which are proportional to concn. at 0·0425 to 0·967 mol % of CuO and 0·05 to 1·2 mol % of CdO. Both waves are better described by the Heyrovský - Ilkovic equation than by the Kolthoff - Lingane equation. For Cd, $E_{\frac{1}{2}}$ is approx. constant and is − 0·904 to − 0·854 V. For Cu, $E_{\frac{1}{2}}$ varies in the indicated concn. range from − 0·3 to − 0·456 V. The usual dependence of $E_{\frac{1}{2}}$ on log $N/2$, where N is the molar fraction of the substance being reduced, is not found. The value of the diffusion current (i_d) is directly proportional to the length of the electrode, and with increase of the temp. from 760° to 875° varies according to the equation $\ln i_d = A - B/T$. C. D. KOPKIN

4004. **Determination of silver in ores.** J. Michal, E. Pavlíková and J. Zýka (Inst. für Erzforschung, Prague). *Z. anal. Chem.*, 1958, **160** (4), 277–279.—The photometric method with Mercupral (Cu^{2+} - disulfiram complex) described previously (*cf.* Michal and Zýka, *Anal. Abstr.*, 1957, **4**, 2121) has been extended to the determination of Ag in ores. *Procedure*—Evaporate the sample (0·2 to 2 g) with HF - $HClO_4$ - HNO_3 (30:5:1) (15 ml) until fuming, cool, moisten with the acid mixture and evaporate again. Heat the residue with H_2O (100 ml), cool and filter. Mix an aliquot of the filtrate containing 10 to 50 μg of Ag with a soln. of Mercupral (100 μg) in benzene (15 ml), dilute with H_2O to about 70 ml and shake for 3 or 4 min. Separate the benzene layer, wash with H_2O, dilute with ethanol to 25 ml, mix, and measure the extinction at 420 mμ. Compare with a calibration curve. A. R. ROGERS

4005. **Analysis for industry. [Colorimetric determination of silver. I.]** R. Goulden (*Ind. Chem. Mfr*, 1958, **34**, 137–138.—Some 22 methods of colorimetrically determining Ag in trace amounts are summarised and discussed. Special attention is given to the use of a specific or selective organic agent, the dithizone procedure being the most important. (30 references.) S.C.I. Abstr.

4006. **Electrometric determination of silver.** R. Z. Kadanov and M. M. Zemyankovich. *Radiotekh. Proizvod.*, 1957, (8), 17–19; *Ref. Zhur., Khim.*, 1958, Abstr. No. 28,407.—For the determination of Ag in silver-plated non-ferrous metals, dissolve the Ag in 3 to 10 ml of HNO_3. Neutralise the soln. with saturated Na_2CO_3 soln. till weakly acid. Insert the electrodes (an amalgamated silver wire and, as standard electrode, an electrode prepared from silver wire, agar jelly, and a paste of Ag_2CrO_4), stir mechanically and titrate with 0·1 or 0·01 *N* NaCl to a zero reading on the galvanometer. The method may also be used for the determination of Ag in alloys and silver cyanide electrolytes.

C. D. Kopkin

4007. **Electrolytically generated silver(II) as a coulometric titrant. [Titration of oxalic acid, cerium(III), arsenic(III) and vanadium(IV).]** D. G. Davis and J. J. Lingane (Harvard Univ., Cambridge, Mass., U.S.A.). *Anal. Chim. Acta*, 1958, **18** (3), 245–252.—Conditions are investigated for the electro-generation of Ag^{2+} with 100% current efficiency. A gold electrode is adopted and a current density > 2 mA per sq. cm. To avoid reduction of Ag^{2+} by water, the supporting electrolyte must be 3 to 7 *M* in HNO_3 and the titration must be conducted at $\simeq 0°$. Decimolar $AgNO_3$ soln. are used. Amperometric end-point detection with platinum electrodes is more generally applicable than the potentiometric method and the necessity of pre-oxidising the electrodes usually arises. The method is used for the coulometric titration of oxalic acid, Ce^{3+}, As^{3+} and V^{4+}.

W. C. Johnson

4008. **Study of losses in assaying [of silver and gold], with radioactive isotopes as tracers.** I. D. Fridman. *Trudy Nauch. I. Gornorazved. Inst. "Nigrizoloto,"* 1957, (24), 151–154; *Ref. Zhur., Khim.*, 1958, Abstr. No. 21,205.—The influence of the nature of the cupels on the losses of Ag and Au in the process of cupellation has been studied by using ^{110}Ag and ^{198}Au. It is established that losses of Ag in ceramic cupels are considerably greater than losses in magnesite and bone-ash cupels, irrespective of their manner of manufacture; the smallest losses of Ag are observed in magnesite - ceramic cupels with 85% of magnesite and in magnesite cupels containing sodium silicate. Cupels of magnesite brick give smaller losses than cupels of magnesite metallurgical powder. The smallest losses of Ag are obtained in cupels prepared from finely ground material. Only deep cupels (8 to 13 mm) ensure the greatest reduction of cupellation losses of Ag; the smallest losses occur in cupels with a central hollow. The decrease in the losses of Ag in deep cupels is due mainly to increase in the capture of base metals in the silver regulus, and also to decreased losses by absorption by the cupel. A change of temp. of the muffle-furnace, even by 20° or 30°, and change of position of the cupels in the furnace, have a marked influence on cupellation losses of Ag. C. D. Kopkin

4009. **Separation of the alkaline earths by chromatography on a cellulose column.** J. Fouarge (Univ., Liége, Belgium). *Anal. Chim. Acta*, 1958, **18** (3), 225–230 (in French).—A technique previously described (*Anal. Abstr.*, 1955, **2**, 2358) is applied to the separation of Ca, Sr, Ba and Ra, radioactive isotopes being used in the investigation. Calcium and Sr are separated by elution with a mixture of methanol, ether and 12 *N* HCl (15 + 5 + 1, by vol.); Ba and Ra are separated by elution with a mixture of methanol and 12 *N* HCl (20 + 1, by vol.). All four elements are separated by the successive use of the two eluents. W. C. Johnson

4010. **Photometric determination of magnesium in aluminium and its alloys with Eriochrome black T.** H. Pohl (Bundesanstalt f. Materielprüfung, Berlin-Dahlem). *Aluminium, Berlin*, 1957, **33** (4), 260–263.—The method is applicable to magnesium contents from 0·001 to 0·5%. Magnesium hydroxide is separated, on $Fe(OH)_3$ as carrier, from NaOH soln. and alloying elements are removed by the extraction of diethyldithiocarbamates and 8-hydroxyquinoline pptn. before the final photometric determination. *Procedure*—Dissolve 1 to 5 g (according to the content of Mg) in 15 to 75 ml of 25% NaOH soln. in a polyethylene beaker. Dilute to $\simeq$ 150 ml, add 1 ml of $FeCl_3$ soln. (1 mg of Fe^{3+} per ml) and set aside overnight. Filter, wash the ppt. with hot water and then dissolve it in 5 ml of dil. HCl (1:12) containing one drop of H_2O_2 (100 vol). Evaporate to dryness, take up in 1 ml of HCl (1:12) and 5 ml of H_2O and dilute to $\simeq$ 150 ml. Adjust the pH to 4·9 $\pm$ 0·2 with 50% Na acetate soln. (6 to 8 ml). Add 5% 8-hydroxyquinoline in methanol (5 to 10 ml), set aside for 30 min. at 60° to 80°, and filter. Transfer the filtrate to a separating funnel and add 1% aq. Na diethyldithiocarbamate (**I**) (20 ml). Shake for 1 min., add 20 ml of $CHCl_3$ and shake for 2 min. Reject the $CHCl_3$ layer and repeat the extraction twice adding 10-ml portions of **I** and 20-ml portions of $CHCl_3$. Wash the aq. phase 5 times with 10-ml portions of $CHCl_3$ and transfer to a beaker. Add 30 ml of buffer (450 ml of 25% aq. NH_3 and 10 g of NH_4Cl to make 500 ml) and 10% KCN soln. (5 ml). (The pH should be 10·6 $\pm$ 0·1 and the vol. 430 to 450 ml.) Transfer to a 500-ml flask and add exactly 20 ml of 0·05% Eriochrome black T soln. in methanol. Dilute to 500 ml, mix, and read the extinction within 30 min. at 546 mμ in a 4-cm cell. A blank must be carried out. Beer's law is obeyed up to 80 μg of Mg per 500 ml.

T. R. Andrew

4011. **Beryllon II as an indicator for complexometric titration.** Sheau-Wei Kwauk. *Acta Chim. Sinica*, 1958, **24** (2), 194–196.—Beryllon II (8:1′:8′-trihydroxy-1:2′-azonaphthalene-3:6:3′:6′-tetrasulphonic acid, tetrasodium salt) is used in the determination of Ca plus Mg in limestone, dolomite, etc., and the efficiency is compared with that of Eriochrome black T. At pH 10, the end-point is clearly noted as the colour changes from blue - violet to violet - red. Titanium, Fe and Al do not form coloured complexes with this reagent at this pH and therefore Ca and Mg can be titrated directly with EDTA in the presence of these metals with K Na tartrate as a masking agent. S.C.I. Abstr.

4012. **Identification and determination of strontium-90, especially in milk. II.** A. Miserez (State Service of Public Hygiene, Berne, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1958, **49** (1),

36–60.—The methods discussed briefly in an earlier paper (*cf. Anal. Abstr.*, 1958, **5**, 2785) are given in detail. S. BAAR

4013. **Determination of small concentrations of barium ions.** N. Z. Kotelkov and M. S. Voshchinskaya. *Trudy Saratovsk. S. Kh. Inst.*, 1957, **10**, 394–398; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,544.—The nephelometric determination of Ba as $BaSO_4$ or $BaSO_3$, with the photo-electric nephelometer constructed by Kotelkov (*Trudy Saratovsk. S. Kh. Inst.*, 1939, **1**, 240), is described. Into each of 5 100-ml beakers place HCl (1:10) (5 ml), 0·01 *N* Na_2SO_4 or $(NH_4)_2SO_4$ (2 ml) and water (8, 6, 4, 2 and 0 ml, respectively), and slowly, with constant stirring, add 0·001 *N* $BaCl_2$ (2, 4, 6, 8 and 10 ml, respectively). After 12 or 15 min. measure the opalescence. The suspensions are stable for 30 min. It is established that more stable (up to 5 hr.) suspensions are obtained with $BaSO_3$ formed as follows. Into each of 10 100-ml beakers place 0·01 *N* Na_2SO_3 (10 ml), water (18, 16, 14, 12, 10, 8, 6, 4, 2 and 0 ml, respectively) and 0·001 *N* $BaCl_2$ (2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 ml, respectively), and measure the opalescence after 10 or 15 min. C. D. KOPKIN

4014. **A new variation of the internal electrolysis method. II. Determination of zinc.** B. Sagortschew, A. Liptschinsky, C. Schejtanow and B. Jordanow (Chem-technol. Inst., Sofia, Bulgaria). *J. prakt. Chem.*, 1957, **4** (5–6), 241–243.—Zinc is deposited from alkaline soln. containing only a slight excess of NaOH. Sodium amalgam in a collodion-impregnated extraction thimble is used as the anode, with copper-plated platinum gauze as the cathode. Deposition is complete in 45 min. A mean error of ± 0·3% is claimed in the range 5 to 100 mg of Zn. T. R. ANDREW

4015. **Application of complexing agents in the photometric determination of zinc and copper with zincon.** R. H. Maier and J. R. Kuykendall (Dept. of Agric. Chem. and Soils, Univ. of Arizona, Tucson, U.S.A.). *Chemist Analyst*, 1958, **47** (1), 4–6.—In the photometric determination of Zn and Cu with zincon (**I**), the absorbance at pH 9·4 and 620 mμ is due to Zn plus Cu, Beer's law being obeyed up to 60 μg per 50 ml. Several complexing agents were found to mask Zn, EDTA being finally selected. Aliquots (25 ml) of the soln. containing ⩾ 60 μg of Cu plus Zn are placed in each of two beakers, and treated with 10 ml of Clark and Lubs buffer, pH 9·4, and 1 ml of reagent (0·13 g of **I** dissolved in 2 ml of *M* NaOH and made up to 100 ml with water). The pH is adjusted to 9·4 with NaOH or HCl, and to one beaker is added 1 ml of 0·025 *M* EDTA. The mixtures are made up to 50 ml and transmittances read at 620 mμ against a reagent blank, results being referred to a standard curve. The mixture without EDTA gives Cu plus Zn, that with EDTA gives Cu only. Iron and Mn interfere; NH_4^+ interfere with the formation of the Zn complex, but not with that of Cu. R. E. ESSERY

4016. **Simultaneous titrations of zinc and cadmium with the "dead-stop end-point."** Sheau-Shya Kao and Wen-Teh Chuang (Dept. of Chem., Peking Univ.). *Acta Chim. Sinica*, 1958, **24** (1), 25–29.—The dead-stop end-point method has been found very convenient in the pptn. titrations of Zn^{2+} and Cd^{2+} with $K_4Fe(CN)_6$ (**I**), an applied voltage of 50 mV being used. In *M* HCl, Zn^{2+} can be quant. pptd. by **I** as $Zn_3K_2[Fe(CN)_6]_2$, while Cd^{2+} remain in soln. After adding $(NH_4)_2SO_4$, Cd^{2+} can be quant. pptd. as $Cd_5(NH_4)_6[Fe(CN)_6]_4$. *Procedure*—Dissolve 0·5 to 0·8 g of sample in 10% HCl. Filter, add conc. HNO_3 (0·5 ml), then evaporate to dryness. Treat the residue with 6 *N* HCl (50 ml). Remove Fe by ether extraction. Boil to remove traces of ether, then cool, and dilute to 250 ml with water. To 50 ml in a beaker add H_2O (10 ml) and 6% $K_3Fe(CN)_6$ soln. (5 drops), then titrate Zn^{2+} with 0·05 *M* **I**, with the dead-stop end-point method. When complete, add $(NH_4)_2SO_4$ (9 g) and continue the titration. Satisfactory results for Zn and Cd in 2 samples of "spongy cadmium" are reported. S. H. YUEN

4017. **Precipitation of cadmium sulphide from acid solutions of thioacetamide.** D. F. Bowersox and E. H. Swift (California Inst. of Technol., Pasadena, Calif.). *Anal. Chem.*, 1958, **30** (7), 1288–1291.—The kinetics of this reaction are discussed and are found to be similar to those for PbS under these conditions, as studied by Swift and Butler (*Anal. Abstr.*, 1956, **3**, 2061). At pH values of < 2 the CdS pptn. is due to hydrolysis of the thioacetamide to H_2S. As the pH is raised, the role of the direct reaction increases until it becomes predominant at values > 4. The use of thioacetamide should be approached with care, since it hydrolyses only slowly even at 90° and cannot produce the condition of saturation commonly achieved with gaseous H_2S. G. S. ROBERTS

4018. **Spectrographic determination of impurities in pig cadmium.** N. A. Porkhunova. *Sb. Trud. Vses. Nauch. Inst. Tsvet. Met.*, 1956, (1), 197–202; *Ref. Zhur., Khim.*, 1958, Abstr. No. 24,877.—In metallic cadmium, Cu is determined by the lines (in A) Cu 3273·0 and Cd 3080; and Pb, Zn and Tl by Pb 3683·0, Zn 3345 and Tl 3519 or 3775·5, with Cd 3649 as comparison. C. D. KOPKIN

4019. **Determination of microgram and submicrogram amounts of boron. I. Absorptiometric determination using curcumin.** G. S. Spicer and J. D. H. Strickland (U.K. Atomic Energy Authority, Royal Arsenal, Woolwich, England). *Anal. Chim. Acta*, 1958, **18** (3), 231–239.—Three methods are described for the determination of B after distillation, as methyl ester, into a soln. of glycerol, NaOH and NaCl. The soln. thus obtained is evaporated and the residue is ignited. In the first two methods this residue is heated, under carefully controlled conditions, with an ethanolic soln. of curcumin, oxalic acid and HCl, and taken to dryness. The rubrocurcumin formed is extracted from the residue and the extinction of the soln. at 555 mμ is measured. These methods are suitable for the determination of 2 to 15 μg and 0·5 to 4 μg, respectively, of B. In the third method a soln. of curcumin in acetone and water is used and, after evaporation with this reagent, the residue is heated with a mixture of *o*-chlorophenol, acetic anhydride and $HClO_4$. After adding ethanol the extinction is measured at 550 mμ and 630 mμ, and the B present is calculated from these values. The coloured substance produced is rubrocyanine. This method serves for the determination of 0·01 to 0·2 μg of B. W. C. JOHNSON

4020. **Fluorimetric determination of boron with morin.** Akira Murata and Fumio Yamauchi (Fac. of Engng, Shizuoka Univ., Oiwake, Hamamatsu). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (2), 231–236.—The yellowish-green fluorescence of

an acetone soln. of borate and morin was applied to the determination of B (0·5 to 12 μg). The intensity of the fluorescence increases in the presence of organic acids such as oxalic, malonic, succinic and phthalic. Other experimental conditions were also examined. The sample soln. is evaporated to dryness in a platinum dish with 0·1 *N* Na_2CO_3 (5 ml). The residue is dissolved in *N* HCl (2 ml) and oxalic acid (0·1%, 1·5 ml), then evaporated with morin soln. (0·02% in ethanol) (1·5 ml) and heated in an oven at 110° for 30 min. The product is dissolved in acetone, filtered and diluted to 25 ml. The fluorescence is measured after 30 min., with the sodium salt of fluorescein (0·0001% soln.) as standard. Any variation in the amount of Na^+ and Cl^- does not cause interference. This method is applicable to the analysis of natural waters without the separation of B. K. SAITO

4021. **Detection of aluminium with alizarin after removal of interfering elements by extraction.** F. G. Zharovskiĭ. *Nauk. Zap. Kiivs'k. Univ.*, 1957, **16** (15), 147–148; *Ref. Zhur., Khim.*, 1958, Abstr. No. 28,418.—A method is described for the detection of Al with alizarin after preliminary removal of V, Ti, Zr and Fe as their N-benzoylphenylhydroxylamine compounds. C. D. KOPKIN

4022. **Mass-spectrographic identification of impurities in aluminium.** S. Floberg and A. Fursey (Chem. Res. Lab., Teddington, Middx). *J. Inst. Met.*, 1957–58, **86** (2); *Bull. Inst. Met.*, **4** (2), 11.—For qual. analysis of impurities in aluminium by a vacuum-spark, double-focusing spectrograph of the Mattauch - Herzog type, cations of the material are produced in an evacuated ion-source assembly by a high-voltage spark between specimen rods of 1 to 2 mm diameter. Masses of 6 to 250 can be recorded at one exposure and 10 exposures can be recorded on one plate. In a specimen of a single crystal of high-purity aluminium containing 0·15% of Cu, 29 elements were detected by the mass spectrometer but only 19 by the emission spectrograph despite repeated analyses specially concentrated on the unidentified elements. No attempt has been made to make accurate quant. analyses by the mass spectrometer. C. H. COWPER-COLES

4023. **Photometric method for the rapid determination of alumina in refractory materials.** H. F. Reich and F. Grabbe (Firma Dr. C. Otto, G.m.b.H., Bochum-Dahlhausen, Germany). *Ber. dtsch. keram. Ges.*, 1957, **34** (7), 236–241.—Modifications in the apparatus and in the preparation of the sample soln. are given for a method reported earlier (*cf.* Giesen *et al.*, *Ber. Tech. Komm. Forschungsinst. Feuerfest. Ind.*, 1953, Report No. 3; *Anal. Abstr.*, 1954, **1**, 1218). J. A. SUGDEN

4024. **Rapid colorimetric determination of aluminium oxide in slags and agglomerates from lead and copper production.** L. N. Krasil'nikova and L. I. Maksal. *Sb. Trud. Vses. Nauch. Inst. Tsvet. Met.*, 1956, (1), 159–164; *Ref. Zhur., Khim.*, 1958, Abstr. No. 21,163.—The reagent used is stilbazo. Fuse 1 g of slag or agglomerate in an iron crucible with 3 g of Na_2O_2 at 650° to 700°, extract the melt with water, dilute to 500 ml, mix and filter. To an aliquot of the filtrate (3 ml for a slag and 5 ml for an agglomerate) add 0·5 *N* H_2SO_4 to pH ≃ 5·4, 0·2 ml of a 5% soln. of ascorbic acid (to reduce Fe^{3+} and Cu^{2+}) and 5 ml of a 0·01% aq. soln. of stilbazo, make up to 50 ml with an acetate buffer soln. (pH 5·4) and measure the extinction with a green filter (530 mμ), with a control sample treated as described as comparison soln. Construct a calibration curve. Beer's law is not obeyed, so that a large number of points should be taken. Interference is caused by Pb, Zn, Ca and SiO_2. The presence of up to 0·5 mg of Cu and up to 1 mg of Fe in the soln. after the reduction with ascorbic acid does not cause interference; when Cu and Fe are both present the determination of Al is not possible. The results obtained agree well with those of the gravimetric phosphate method. The determination takes 40 to 60 min. C. D. KOPKIN

4025. **Polarographic determination of the oxides of aluminium, iron and titanium in aluminosilicate materials.** E. V. Ermolaeva and L. A. Korobka. *Byull. Nauchno-Tekh. Inform. Vses. Nauch. Inst. Ogneuporov*, 1957, **2**, 84–89; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,611.—A method is described for the direct polarographic determination of Al, Fe and Ti in aluminosilicates (chamottes, clays and kaolins). Heat 0·2 g of sample with HF and H_2SO_4 to remove SiF_4, fuse the residue with $NaHSO_4$ or $KHSO_4$, warm the melt with conc. HCl and precipitate the oxides with aq. NH_3. Wash the ppt., dissolve it in HCl and take 40, 20 and 20 ml of the soln. for the determination of Al, Fe and Ti, respectively. Polarograph Ti from a soln. of the tartrate complex at pH 1·2 to 1·3 at −0·9 V, Fe from a soln. of the citrate complex at pH 9 to 9·6 at −0·1 V (maintaining the pH to Tropaeolin OO, which at the same time serves to depress the maxima), and Al in a basal soln. of NaCl or KCl at pH 3·5 to 3·8 and −1·75 V in the absence of complexing reagents. The max. error of the determination is Al_2O_3 0·67, Fe_2O_3 0·27, and TiO_2 0·25% (abs.). C. D. KOPKIN

4026. **Separation of gallium from zinc, copper, cobalt, nickel and iron by ion exchange.** A. I. Zelyanskaya and N. V. Bausova. *Izv. Vost. Fil. Akad. Nauk SSSR*, 1957, (7), 51–53; *Ref. Zhur., Khim.*, 1958, Abstr. No. 21,168.—The separation of Ga from Ni, Co, Zn and Cu by ion exchange is based on the amphoteric properties of Ga and the ability of Ni, Co, Zn and Cu to form stable ammonia complexes. To 100 ml of soln. add conc. aq. NH_3 (15 ml) and 2 *N* NaOH (10 ml), and allow it to pass through a column (diam. 1 cm, height 50 cm) of the cationite SBS (Na form) (grain size 0·25 to 0·5 mm; loaded to a height of 25 cm) at a rate of 5 ml per min. All the Ga passes through the column, while Ni, Co, Zn and Cu are quant. adsorbed by the cationite. Wash the cationite with 100 ml of a soln. containing 10 ml of conc. aq. NH_3 and 5 ml of 2 *N* NaOH. Evaporate the eluate and wash soln. to 25 ml, neutralise with 6 *N* HCl till weakly acid to methyl orange and determine Ga polarographically in the soln. in the presence of 0·1 *M* Na salicylate. Under the conditions indicated, Fe is also quant. adsorbed by the cationite, and does not interfere in the separation of Ga. C. D. KOPKIN

4027. **Polarography of indium.** S. P. Bukhman and P. I. Zabotin. *Izv. Akad. Nauk KazSSR, Ser. Khim.*, 1957, (2 [12]), 58–62; *Ref. Zhur., Khim.*, 1958, Abstr. No. 28,422.—The influence of various factors on the polarographic behaviour of In is studied. The reduction wave due to In in a basal soln. of H_2SO_4 in the presence of gelatin is poorly developed, since it is not far from the wave due to H; but it becomes more distinct if the background is "subtracted." The wave due to In appears at

−0·9 to −1·1 V *vs.* the S.C.E., and the wave height is proportional to the concn. of In in the soln. With increase of the concn. of H_2SO_4 the $E_{\frac{1}{2}}$ of In moves towards more electro-negative values; with a H_2SO_4 concn. of >10 g per litre the wave due to In coalesces with that due to H. The addition of NaCl to the H_2SO_4 soln. causes the wave due to In to appear at − 0·55 to − 0·65 V *vs.* the S.C.E.; increase of concn. of NaCl causes the value of $E_{\frac{1}{2}}$ to move towards more electro-negative values and the height of the wave to increase to a definite max. at a given concn. of In. The waves due to In are very sharp, even in the absence of gelatin, and the wave height is proportional to the concn. of In; change of the H_2SO_4 concn. in the soln. from 0 to 240 g per litre does not influence the wave height.
C. D. KOPKIN

4028. **Determination of indium in sphalerite concentrates by amperometric titration with Complexone [III].** B. S. Tsȳvina and V. M. Vladimirova. *Zavod. Lab.*, 1958, **24** (3), 278–280.—Before the titration as previously described (*cf.* Vladimirova, *Anal. Abstr.*, 1958, **5**, 2557), the In together with Ga present in soln. of sphalerite concentrate in 5 *N* HBr is extracted by means of butyl acetate, and In is selectively re-extracted from the extract by means of dil. HCl. In the absence of Ga, water is used for the re-extraction. G. S. SMITH

4029. **Co-precipitation of tervalent thallium with quadrivalent manganese hydroxide.** G. V. Efremov and I. P. Alekseeva. *Uch. Zap. LGU*, 1957, (211), 87–91; *Ref. Zhur., Khim.*, 1958, Abstr. No. 14,168.—In studying the co-pptn. of Tl^{3+} with $Mn(OH)_4$ from soln. of 1 litre at concn. of 0·34 to 3·4 μg of Tl per ml, it is shown that complete removal of Tl takes place at a Tl to Mn ratio of 1:10 (3·4 μg of Tl per ml), 1:16 (1·7 μg of Tl per ml), 1:80 (0·85 μg of Tl per ml) and 1:100 (0·34 μg of Tl per ml); the presence of free alkali lowers the co-pptn. of Tl. To the soln. containing Tl add the necessary amount of $MnSO_4$, 10 drops of 30% H_2O_2, and then, with stirring, 2 *N* NaOH, first till the soln. is neutral to methyl orange and then the amount necessary to precipitate Mn and Tl, and warm to 70° to obtain a completely clear soln. Set aside for 3 hr., filter, and dissolve the ppt. in a small quantity of conc. HCl in the presence of H_2O_2. Determine Tl photometrically with methyl violet.
C. D. KOPKIN

4030. **Quantitative volumetric determination of small amounts of thallium as thallium reineckate.** I. L. Bagbanlȳ and T. R. Mirzoeva. *Uch. Zap. Azerb. Univ.*, 1957, (4), 35–45; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,552.—The method is based on the oxidative titration of thallium reineckate with KIO_3 soln. Acidify 5 or 10 ml of soln. with H_2SO_4 (1:4) to obtain (after addition of reagent) an acidity of 2 *N*, add 1 to 1·5 ml of a freshly prepared 2·5% soln. of Reinecke's salt for each mg of Tl expected, and warm for 20 min. on a water bath at 50° or 60°. Filter off the ppt., wash it three or four times with water and, after transference to the original beaker, decompose it by warming with 5% NaOH soln. on a water bath. Add 10 ml of water, 10 ml of HCl (sp. gr. 1·19) and 10 ml of benzene, and titrate with KIO_3 soln. till the benzene layer is no longer pink. This method is more rapid and accurate than other titrimetric methods, and enables 0·2 mg of Tl in 25 ml of soln. to be determined. Cations of the first three analytical groups do not interfere. C. D. KOPKIN

4031. **Separation of lanthanum from other cerite earths excluding cerium.** P. Jayarama Reddy, D. V. N. Sarma and B. S. V. Raghava Rao (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1958, **160** (6), 426–429 (in English).—In the absence of Ce, La can be separated from the rare earths by controlled pptn. with K_2CrO_4. *Procedure*—To 10 ml of soln. in dil. HCl containing not more than 0·05 g of La_2O_3, add 1% Na acetate soln. (40 ml) followed by 1% K_2CrO_4 soln. (40 ml) and adjust the pH to 5·7. Dilute the soln. to 100 ml, digest on a water bath for 1 hr. with continuous stirring, cool and filter. Wash the ppt. with water of pH 5·7 then dissolve it in 0·05 *N* HNO_3. Neutralise the soln. with KOH and repeat the pptn. under the same conditions. Dissolve the ppt. in dil. HCl and determine La as La_2O_3 after two pptn. as oxalate. Use aq. NH_3 and acetic acid for the pH adjustments. G. BURGER

4032. **Determination of carbon dioxide in automotive exhaust by means of infra-red filter-photometer.** J. L. Parsons, J. C. Neerman, J. R. Lifsitz and F. R. Bryan (Sci. Lab., Ford Motor Co., Dearborn, Mich., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1055–1057.—Details are given of an interference filter-photometer designed for measuring CO_2 absorption at 4·29 μ and utilised for monitoring a petrol engine exhaust. Concn. of CO_2 from 1·0 to 18% by vol. are determined within 10% of the amount present. The values tend to be higher than those obtained by Orsat determinations.
K. A. PROCTOR

4033. **Rapid determination of silicon in ferrosilicon.** S. Velken (Elektrokemisk A/S, Kristiansand S., Norway). *J. Iron St. Inst.*, 1958, **188** (2), 119–121.—The finely ground ferrosilicon (0·2 g) is fused with 2·5 g of K_2CO_3 - Na_2O_2 (1:1, by wt.). The melt is extracted with hot water to which 35 ml of HNO_3 (sp. gr. 1·4) is added, followed by KCl (6 g). Then 40% HF (10 ml) and a little paper pulp are stirred in and the soln. is cooled (in ice water) for 10 to 15 min. with occasional stirring. To accelerate the quant. pptn. of the K_2SiF_6 it may be advantageous to stir with a motor fitted with a plastics stirrer; 3 min. at 500 to 1000 r.p.m. will be sufficient. The soln. is filtered on a paper-pulp pad. The entire residue is transferred to the pad and washed with cold aq. KCl (20%), as little washing soln. as possible being used, preferably < 100 ml, until 10 ml of the wash soln. becomes alkaline to methyl red on addition of one drop of 0·25 *N* NaOH. The ppt. is transferred to an Erlenmeyer flask with 50 ml of hot water and titrated with 0·25 *N* NaOH in almost boiling soln. to a pink colour, with 10 drops of phenolphthalein soln. (1%) as indicator. The only element likely to be present in ferrosilicon in amounts sufficient to affect the result is Al, but concn. up to 3% are not detrimental. Reproducibility is good and 12 determinations of an official sample of ferrosilicon (certificate value Si 75·60%) gave an average of 75·89%, with a standard deviation of ±0·13. A commercial sample analysed in 12 different laboratories gave 77·46% of Si, with a standard deviation of ±0·36. A wet method for the decomposition of ferrosilicon with HNO_3 and HF is also described. J. M. JACOBS

4034. **Rapid determination of silicon and aluminium in ferrosilicon containing 75 to 90 per cent. of silicon.** J. Kadlec and J. Boch (SONP, Kladno, Czechoslovakia). *Hutn. Listy*, 1958, **13** (1), 57–58.—*Silicon*—To the sample (1 g) in a

platinum dish add H_2SO_4 (10 ml) and 40% HF (15 ml). Cover the dish and after 2 min. add HNO_3 till the sample is decomposed. Wash the cover and evaporate the soln. to dryness and ignite at 900° in an electric furnace (15 min.). *Aluminium*—Fuse the residue with $KHSO_4$, filter and separate Al, by alkaline treatment, from interfering elements (Fe, Mn, Ti, Ca, Mg, etc.). Neutralise the soln. of Al^{3+} with HCl, add buffer soln. (20 ml) (500 g of Na acetate, 20 ml of glacial acetic acid, and H_2O to 1 litre), 20 ml of 0·05 *M* EDTA (disodium salt) and a 4% soln. of salicylic acid in ethanol (3 to 4 ml). Heat for a short time and titrate at 50° with 0·05 *M* $FeCl_3$ till a red colour appears, or potentiometrically. The whole procedure is completed within 3 hr. The Al can also be determined gravimetrically as phosphate. J. ZÝKA

4035. **The determination of silicon in ferroboron.** E. S. Dzhaparidze and O. D. Bershadskaya. *Trudy Inst. Metalla i Gor. Dela. Akad. Nauk, GruzSSR*, 1958, **8**, 251–252; *Ref. Zhur. Khim.*, 1958, Abstr. No. 35,920.—It has been shown that the indirect determination of the sum of Si and B can be carried out by the loss in weight of these elements as BF_3 and SiF_4 by the action of HF on ferroboron.
W. ROUBO

4036. **Gamma-spectrometric and radiochemical analysis for impurities in ultra-pure silicon.** B. A. Thompson, B. M. Strause and M. B. Leboeuf (General Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1023–1027.—Some 29 elements have been determined, mostly in the parts per thousand million range, in transistor-grade silicon, by using both gamma spectrometry and radiochemical separations with beta counting. The impurities are classified into long-lived and short-lived elements according to their half-lives after subjection to neutron activation. Various neutron sources are compared and discussed. Activation analysis seems to be the best analytical procedure which can be applied on a semi-routine basis for the determination of many of the more important elements in transistor production.
K. A. PROCTOR

4037. **Colorimetric determination of silica in ores and agglomerates.** I. I. Tokarev and A. I. Novachok. *Trudy Nauch.-Tekh. Ob. Chernoĭ Metallurg., Ukr. Resp. Pravl.*, 1956, **4**, 115–118; *Ref. Zhur., Khim.*, 1958, Abstr. No. 24,823.—A photometric method for the determination of SiO_2 as the complex silicomolybdenum blue, after fusion with Na_2CO_3 and solution of the SiO_2 in alkali, is described. The error of the determination is ±0·35% (abs.). C. D. KOPKIN

4038. **The decomposition of silicates with ammonium fluoride.** N. A. Tananaev and S. I. Smȳshlyaev. *Trudy Ural'sk. Politekh. Inst.*, 1957, (69), 101–106; *Ref. Zhur., Khim.*, 1958, Abstr. No. 21,201.—It has been established that the completeness of the decomposition of silicates by the action of NH_4F is satisfactory for their qual. analysis. Heat the finely ground sample (≃ 0·1 g) with a fivefold excess of powdered NH_4F in a platinum crucible at 300° to 400° for 2 or 3 min. A second treatment with NH_4F leads to a more complete decomposition, without greatly increasing the time required. To obtain the most accurate results, the treatment with NH_4F may be carried out several times in 10 to 15 min. C. D. KOPKIN

4039. **Isotopic spectrographic analysis of lead by a photometric method.** A. G. Zhiglinskiĭ. *Optika i Spectroskopiya*, 1957, **3** (1), 9–15; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,604.—An isotopic method was developed for the determination of Pb (0·5 to 2 mg) in a concn. range of 10 to 100% after conversion into PbI_2 on the basis of the relation between the concn. of the isotope and the intensity of the components of the superfine structure. A hollow iron cathode carrying 40 to 80 mA current served as the light source. Argon was used as the charge carrier. The optical system was that described by Kaliteevskiĭ and Chaĭka [*Vestn. Leningrad Univ.*, 1956, **11** (4), *Ser. Fiz. i Khim.*, 1956, (1), 9]. The analyses were based on the line 4058 Å and the photometric arrangement included a multiplier (FEU–17) cooled with liquid air. The intensity (I) of isotopic components $^{206, 207, 208}Pb$ was calculated from the equations—

$$I_{207} = 3z, \quad I_{206} = y - 0{\cdot}017x - 0{\cdot}065z,$$
$$I_{208} = 0{\cdot}97x - 1{\cdot}41z - 0{\cdot}017y,$$

which were obtained from parameters of 15-mm wide dispersions according to Fabry-Perot standard from Pb I 4058 Å and A II 4053 Å bands. The precision of the method was ≃ 4%.
C. D. KOPKIN

4040. **Dithizone method for determination of lead in monazite.** R. A. Powell and C. A. Kinser (Geol. Survey, Washington, D.C., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1139–1141.—In the procedure given, the sample (≃ 50 mg) is decomposed first with hot conc. H_2SO_4 and then with dil. HNO_3. The hot soln. is filtered and any residue (after ignition at 500°) is treated with HF and HNO_3 and the soln. finally obtained is added to the main filtrate, the vol. of which is then made up to 100 ml. The lead is determined in a 10-ml aliquot (≡ ≯ 20 mg of Pb); Th and rare earths (as phosphates usually) are masked with Na citrate and KCN, whilst Fe^{3+} are reduced with H_2SO_3. After adjusting the pH to 9·2, Pb is extracted several times into a $CHCl_3$ soln. of dithizone, from which it is stripped into dil. HNO_3 and then re-extracted into a standard soln. of dithizone in $CHCl_3$. The extinction of the Pb - dithizone complex is measured at 520 mμ in a 1-cm cell against a water reference soln. If an appreciable amount of Bi is present, the Pb should be removed from the dithizone extract with a buffer soln. (pH 3·4) instead of the dil. HNO_3. For contents of Pb from 0·04 to 0·6% (nine samples) reproducibility and accuracy are very good.
W. J. BAKER

4041. **Determination of micro amounts of lead in metallic indium.** A. I. Volkova and N. N. Zakharova. *Ukr. Khim. Zhur.*, 1957, **23** (4), 530–532; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,555.—In this determination, collectors are used to obtain analytical concentrates of Pb. As collectors, Ca oxalate, MnO_2 and $BaCrO_4$ have been tested. Best results are obtained with $BaCrO_4$, which in acetic acid medium carries down Pb quantitatively (In remains in soln. under these conditions), and forms mixed crystals with it. With a single pptn. of Pb with $BaCrO_4$, In is observed in the ppt. After re-pptn., only traces of In (10 to 30 μg) are found in the ppt. Such amounts of In are easily held in soln. by citrates, and do not interfere in the extraction of Pb with dithizone at pH 8 to 8·5. The sensitivity of the determination is 3 to 5 μg of Pb in a 0·1-g sample. The analysis takes 5 hr.
C. D. KOPKIN

4042. **Photometric determination of titanium by extraction as tributylammonium titanium sulphosalicylate.** M. Ziegler, O. Glemser and A. von Baekmann (Univ. Göttingen, Germany). *Z. anal. Chem.*, 1958, **160** (5), 324–332.—A soln. of the sample, buffered to a pH of 2·4 to 4 with Na acetate - acetic acid, is shaken with sulphosalicylic acid and tri-*n*-butylammonium acetate. The titanium complex is extracted with $CHCl_3$ and the extinction measured at 400 mμ. Beer's law is followed in the region 0 to 200 μg of Ti. If Fe^{III} is present in a proportion Fe:Ti > 50:1, it must be reduced to Fe^{II}. Ions that do not interfere include Ni^{2+}, Co^{2+}, Mn^{2+}, Cr^{3+}, Cd^{2+}, Pb, Ca and Cu^{2+}. When Al is present a larger amount of buffer is needed. Vanadyl salts may be present in amounts up to 2 mg. Tungstates must first be removed as tungstic acid and molybdates extracted with $CHCl_3$ after addition of thioglycollic acid; bismuth salts hydrolyse and are filtered off. The method is suitable for the determination of Ti in steel. The error (from 40 determinations) is ≃ 2%.
G. BURGER

4043. **Quantitative X-ray-spectrographic determination of titanium by secondary spectra.** A. S. Ivollov and N. F. Losev. *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1957, **21** (10), 1465–1468; *Ref. Zhur., Khim.*, 1958, Abstr. No. 28,432.—A method is evolved for the determination of Ti in ores at concn. of 0·7 to 50% of TiO_2, based on the use of the X-ray spectrograph of Blokhin (*cf. Zavod. Lab.*, 1950, **16**, 681, 941). Place the finely ground ore (use a quartz-based ore, up to 70% of SiO_2), mixed with a buffer and a binding agent, on an aluminium plate, press, and ignite till the binding agent is burnt off. Prepare standards by successive dilution of ilmenite with the indicated buffer. Excite the Ti spectrum by irradiation from a Cr target run at 25 kV and 15 mA. For the analytical line use Ti = $K_{\alpha 1}$ at the second order of reflection. The mean relative error of the determination is 10%. Eight to ten analyses can be carried out in one working day.
C. D. KOPKIN

4044. **Determination of titanium in coal ash.** F. M. Kessler and L. Dočkalová. *Sbírka Prací Výzkumn. Úst.*, 1957, **A8** (17–26), 188–213; *Ref. Zhur., Khim.*, 1958, Abstr. No. 28,434.—A photometric method is described, based on measurement of the extinction of the yellow compound of Ti^{4+} with H_2O_2 in a 5% H_2SO_4 medium, and a polarographic method, based on measurement of the height of the wave due to Ti in a basal soln. of H_2SO_4 and tartaric acid. In the polarographic method, a direct proportionality between the height of the wave and the concn. of Ti is observed only up to a Fe:Ti ratio of 12. The optimum conditions for the electrolytic removal of Fe from coal ash soln. are described. The polarographic method is more complicated and takes longer, but is suitable for the determination of 0·2 to 0·8% of TiO_2 in the presence of > 0·05% of V (lignite ash). The photometric method is simpler, more rapid, does not require removal of Fe and gives satisfactorily accurate results.
C. D. KOPKIN

4045. **Arsenate method for the iodimetric determination of titanium in the presence of aluminium.** G. B. Shakhtakhtinskiĭ and A. M. Mukimov. *Trudy Azerb. Ind. Inst.*, 1957, (16), 86–93; *Ref. Zhur., Khim.*, 1958, Abstr. No. 24,778.—The method is based on pptn. of $Ti(OH)AsO_4$ in a weakly acid medium (1% in H_2SO_4 and 2% in HCl or HNO_3) with 0·5 *N* Na_2AsO_4 or $(NH_4)_2AsO_4$ at 70° to 80°, washing the ppt. with 2% NH_4Cl soln., solution in dil. H_2SO_4 (1:2·5), addition of KI and titration of the iodine liberated with $Na_2S_2O_3$ soln. in the presence of benzene or chloroform. Under these conditions Al is not pptd. by arsenate, so that the method does not require preliminary removal of Al and may be used in a wide range of ratio of Al to Ti. One determination takes 30 to 45 min.
C. D. KOPKIN

4046. **Determination of titanium in presence of niobium by differential spectrophotometry.** R. A. Guedes de Carvalho (Lab. KUDI, Rua Miguel Bombarda 199, Porto, Portugal). *Anal. Chem.*, 1958, **30** (6), 1124–1127.—The formation of the Ti-H_2O_2 complex is the basis of this method for the determination of Ti in ilmenites. A correction factor, which is separately determined in H_2SO_4, must be applied when the content of Nb is > 5%. The use of two standards for each spectrophotometric determination increases the accuracy.
K. A. PROCTOR

4047. **Vacuum-fusion determination of oxygen and hydrogen in titanium.** E. L. Zakharov. *Byull. Tsvetn. Metallurg.*, 1957, (14), 27–33; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,613.—The apparatus is described. It is established that the most effective heat insulator is graphite powder of grain size 0·074 mm. When analysing titanium in an iron crucible with and without addition of Sn and with an iron sinker for the samples, non-reproducible results were obtained, because of floating and evaporation of titanium. It is necessary to use a carbon container (height 10 mm, external diam. 5 mm, internal diam. 3·5 mm, wt. 0·3 to 0·4 g); then the relative error in the determination of O is ± 1%, and of H 5 to 10%.
C. D. KOPKIN

4048. **Determination of zirconium in titanium alloys using *p*-bromo- or *p*-chloro-mandelic acid.** R. A. Papucci and J. J. Klingenberg (F. C. Broeman and Co., Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1062–1064.—From 0·1 to 10% of Zr in titanium alloys can be determined, to within 0·1 to 2%, by dissolution of the sample (0·25 to 2 g) in HCl (1 + 4) and pptn. of Zr with a 12% excess of solid *p*-bromo- or *p*-chloro-mandelic acid at 80° to 85° (for > 2% of Zr two pptn. are made). The ppt. is ignited at 1000° and weighed as ZrO_2. The final result includes any Hf present. If the content of Zr of the sample exceeds ≃ 0·75%, the insol. residue of W during the initial dissolution should be collected and analysed for retained Zr.
W. J. BAKER

4049. **Separation of zirconium and hafnium by differential reduction of their tetrachlorides.** I. E. Newnham (Div. of Ind. Chem., C.S.I.R.O., Melbourne, Australia). *J. Amer. Chem. Soc.*, 1957, **79**, 5415–5417.—The method (not described in a form for analytical use) depends on the reduction of $ZrCl_4$ with zinc powder *in vacuo* at 400° to 450°; $HfCl_4$ is not reduced and sublimes as an Hf concentrate. The residual $ZrCl_3$ disproportionates at 550° when $ZrCl_4$ sublimes.
C. A. SLATER

4050. **Determination of low concentrations of hafnium in reactor-grade zirconium metal and zirconium alloys by neutron activation analysis.** W. D. Mackintosh and R. E. Jervis (Atomic Energy of Canada, Ltd., Chalk River, Ontario, Canada). *Anal. Chem.*, 1958, **30** (7), 1180–1182.—Four

radionuclides, which are produced by thermal neutron activation of Hf, form the basis of two analytical methods for determining Hf at concn. of < 200 p.p.m. In one method which is simple and rapid, but must be performed at the reactor site, ^{179}Hf (half-life, 19 sec.) is used. In the other method, which can be carried out anywhere, ^{181}Hf or ^{175}Hf is used. At a concn. of 60 to 120 p.p.m. the coefficient of variation is ± 10%. The methods are sensitive to about 10 p.p.m. of Hf.

K. A. PROCTOR

4051. **Detection [determination] of uncombined oxygen in zirconium metal.** L. Silverman and W. Bradshaw (Atomics International, Canoga Park, Calif., U.S.A.). *Anal. Chim. Acta*, 1958, **18** (3), 253–258.—The sample of zirconium is dissolved, *in vacuo*, in an aq. soln. of HF and HCl in an adaptation of an apparatus previously described (*Anal. Abstr.*, 1955, **2**, 3342). The evolved O is dissolved in an aq. mixture of $MnSO_4$, KI and NaOH, which is subsequently acidified, and the liberated iodine is extracted with *o*-xylene. Absorptiometric examination of the soln. of iodine in *o*-xylene provides a measure of the dissolved O originally present in the sample. The method is applied to samples containing 0·06 to 0·22% (50 to 170 μg) of O.

W. C. JOHNSON

4052. **Detection of thorium and uranium.** J. S. Fritz and E. C. Bradford (Iowa State Coll., Ames, U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1021–1022.—Quadrivalent Th (< 5 μg, in a limiting dilution of 1 in 5 × 10^5) and U^{VI} (< 6 μg, in a limiting dilution of 1 in 4 × 10^5) can be detected in aq. soln. containing EDTA, and buffered to pH 8 (triethanolamine), by addition of one drop of a 3 × 10^{-4} *M* soln. of pure arsenazo, which gives a violet colour with Th and a blue colour with U. When both elements are likely to be present, or U is being tested for, an initial extraction of uranyl diethyldithiocarbamate into benzene is made, and the test is then made on the residue after removal of benzene from the non-aqueous phase. Beryllium, Cr^{3+}, F^-, WO_4^{2-}, VO_3^-, oxalate and silicate interfere in the detection of Th, whilst large amounts of VO_3^-, $B_4O_7^{2-}$ and phosphate interfere in the test for U. Interference by any Bi, Cu, Co, Hg, Ag or Sn co-extracted with the U can be suppressed by addition of a drop of thioglycerol (0·08 *M*) before the arsenazo.

W. J. BAKER

4053. **The analysis of thorium - magnesium binary alloys.** G. W. C. Milner and J. W. Edwards (A.E.R.E., Harwell, Berks.). A.E.R.E. Report C/R 2527, 1958, 5 pp.—Procedures are presented for the determination of Th and Mg in their binary alloys. Thorium is determined by direct titration with EDTA (disodium salt) at pH 2·5 to 3, with xylenol orange as indicator. Magnesium is also titrated at pH 10·3 after pptg. the Th as its peroxide in acid soln. by the addition of $HClO_4$ and heating with 100-vol. H_2O_2 soln. The indicator used is Solochrome black B. The error in 4 determinations on alloys with a content of Th of 1·14 to 50·0% was ≯ ±0·2% for Th and for Mg in 3 determinations +0·04 to +0·6%.

N. E.

4054. **Complexometric determination of thorium in the presence of cerium.** S. Lupan. *Rev. Chim., Bucharest*, 1958, **9** (2), 101–102.—The ppt. of the oxides of Th and Ce is dissolved by heating with HCl plus a few crystals of KI. After evaporating to dryness, the residue is moistened with 0·5 ml of conc. HCl and diluted with a little water to 50 ml, when it should dissolve completely. Ethanol (10 to 20 ml) is added, and the soln. is boiled until decolorised. A little more ethanol is added, the soln. is cooled, diluted to about 250 ml, and 4 to 5 drops of catechol violet soln. (0·1%) are added. It is then titrated with EDTA until yellow. Amounts of 1 mg to 18·6 mg of Th in the presence of 500 mg of Ce can be determined. Lanthanum, Pr and Nd do not interfere; other possible interfering elements are eliminated in the pptn. and purification of oxides of Th and Ce.

H. SHER

4055. **Determination of water vapour in nitrogen. Thermal conductivity measurement of hydrogen liberated from calcium hydride.** H. W. Linde and L. B. Rogers (M. I. T., Cambridge, Mass., U.S.A.). *Anal. Chem.*, 1958, **30** (7), 1250–1252.—Water vapour in nitrogen in the concn. range 200 to 2000 p.p.m. can be determined in ≃ 10 min. by reaction with calcium hydride at 235°. At a lower temp. the results are more erratic. Alcohol vapours interfere, but in the absence of water vapour the alcohols themselves can be determined. The results are not sufficiently reproducible for precise routine determinations.

K. A. PROCTOR

4056. **New microscopic reaction for ammonia.** M. Oosting (Anal. Inst., T.N.O., Holland). *Chem. Weekbl.*, 1958, **54** (10), 132.—Ammonia is liberated by adding a drop of 4 *N* KOH to a drop of soln. in a micro-desiccator containing a microscope slide on which is a drop of 70% $HClO_4$. After 10 min. some of the water on the slide is evaporated on a warm plate. Characteristic crystals (illustrated) are seen under the microscope.

P. RENTENAAR

4057. **Chromatographic analysis of gas mixtures containing nitrogen, nitrous oxide, nitric oxide, carbon monoxide and carbon dioxide.** R. N. Smith, J. Swinehart and D. G. Lesnini (Chem. Dept., Pomona Coll., Claremont, Calif.). *Anal. Chem.*, 1958, **30** (7), 1217–1218.—The gases can be separated and determined in ≃ 10 min. at 115° on a 10-ft. column filled with two layers of silica gel separated by about 8 in. of iodine pentoxide, which oxidises the CO to CO_2 and the NO to NO_2 with the liberation of iodine. The nitrogen peak height is affected by the presence of both CO and NO, and this makes fairly extensive calibration necessary. Simple gas sampling and transfer units are described.

K. A. PROCTOR

4058. **Determination of nitrogen dioxide by gas - solid chromatography.** S. A. Greene and H. Pust (Aerojet-General Corp., Azusa, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1039–1040.—Separation and determination of NO_2 can be carried out by passing the sample through a water-treated mol.-sieve column of Al_2O_3 or silica gel (10 ft. long, 20 to 40 mesh) at 23°, whereby NO_2 is converted into NO. The resulting wave form is congruent with that of pure NO, and is amenable for quant. analysis, *viz*, pressure (in const.-vol. bulb) *vs.* peak height. This procedure avoids the complication of oxidation of organic partitioning liquids. The apparatus used was described by Greene *et al.* (*Anal. Chem.*, 1956, **28**, 1369).

W. J. BAKER

4059. **Colorimetric determination of nitrites with 3-methyl-1-phenylpyrazolone and its derivatives.** P. V. Kristalev and L. B. Kristaleva. *Trudy Tomsk. Univ.*, 1957, **145**, 73–76; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,573.—The method is based on the formation of a yellow colour by the reaction of NO_2^- with 3-methyl-1-phenylpyrazolone (**I**). To

the soln. to be analysed add 1 or 2 ml of a 5% ethanolic soln. of **I** and 20 or 25 drops of 10% acetic acid, make up to 10 ml and after 10 to 15 min. measure the extinction with a blue filter. The sensitivity of the method is 0·005 mg of NO_2^- per ml. The colour formed is stable for 2 or 3 days. No interference is caused by the presence of NO_3^-, Cl^-, SiO_3^{2-}, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+} or Al^{3+}. The influence of Fe^{3+} is removed by the addition of F^-. C. D. KOPKIN

4060. **Gravimetric method for the determination of small amounts of phosphorus.** C. Gheorghiu and E. Rădulescu (Univ. C. I. Parhon, Bucharest). *Rev. Chim., Bucharest*, 1957, **8** (12), 779–780.—By the method described, P is determined under macrogravimetric conditions, but it is claimed that amounts of 0·1 mg can be determined rapidly with an error of the order of 1 μg. *Procedure*—To 50 ml of a neutral or faintly acid (HNO_3) soln. containing 0·5 to 2·0 mg of P_2O_5 is added the requisite amount of ammonium molybdate reagent. The ppt. is allowed to stand for 15 min., filtered off and washed with 1% ammonium nitrate soln. until free from reagent, then dissolved in a minimum amount of aq. NH_3. The soln., adjusted to ≃ 25 ml, is treated with H_2S until it becomes intensely red, then diluted to between 50 and 80 ml and treated with a soln. of penta-amminochromium chloride (**I**), about 0·3% excess, until a clear red soln. is obtained. The mixture is stirred for 2 to 3 min. and the ppt. of $[MoS_4][Cr(NH_3)_5Cl]$ is filtered off and washed with a soln. containing 0·8 g of **I** and 0·5 ml of aq. NH_3 per litre, followed by 94% ethanol and ether. The ppt. is then vacuum-dried for 5 to 10 min.

H. SHER

4061. **Determination of total phosphorus in granular zinc (arsenic-free) by visual colorimetry.** I. A. Korobova and N. G. Velichko. *Trudy Ural'sk. Politekh. Inst.*, 1957, (69), 137–142; *Ref. Zhur., Khim.*, 1958, Abstr. No. 24,827.—A method is described for the determination of P by the intensity of the colour of the blue (reduced) form of molybdovanadophosphoric heteropoly acid. The method is more rapid than the normal methods and requires smaller amounts of reagents. Dissolve an accurately weighed 1-g sample by warming with HNO_3 (sp. gr. 1·2, 8 to 10 ml), boil to remove oxides of N, add 3 to 5 drops of 0·5% $KMnO_4$ soln. and 1 or 2 drops of 3% H_2O_2, boil for 1 or 2 min., cool and dilute to 10 ml in a measuring cylinder (soln. *A*). Place 1 ml of soln. *A* and 1 ml of a standard soln. containing 5×10^{-7} g of P in separate measuring cylinders, add 1% aq. NH_3 dropwise to each till a ppt. of $Zn(OH)_2$ appears and 1 or 2 drops of H_2SO_4 (1:3), dilute to 2 ml, add 3 drops (0·1 ml) of a previously prepared soln. of ammonium molybdate and vanadate [to 100 ml of 0·3% $NaVO_3$ soln. add 100 ml of 10% $(NH_4)_2MoO_4$ and 80 ml of 50% HNO_3], mix, and after 5 min. add 10 drops of H_2SO_4 (1:3), 3 drops of 1% $SnCl_2$ soln. and 10 drops of satd. Na acetate soln. and immediately compare the intensities of the colours of the soln. The presence of SiO_2 does not cause interference. C. D. KOPKIN

4062. **Determination of phosphate in uranium ores, concentrates and liquors via an EDTA titration.** K. F. Sporek (Eldorado Mining & Refining, Ltd., Res. & Development Div., Ottawa, Canada). *Chemist Analyst*, 1958, **47** (1), 12–13.—The phosphate (0·1 to 0·2 g) is evaporated with HBr to remove As as tribromide, and the residue is heated with HNO_3 to remove Br, diluted to 100 ml, and filtered. Other interfering cations are then removed by passage of the filtrate through a column (1 in. × 8 in.) of Amberlite IR-120 regenerated with HCl (1:2), and washing the column with water till the eluate is neutral to methyl orange; the eluate and washings are then treated with 25 ml of aq. NH_3 (1:1). Alternatively, the phosphate is pptd. as ammonium molybdophosphate, the ppt. is washed with NH_4NO_3 soln. till free from interfering cations when tested with Eriochrome black T, then dissolved in 25 ml of aq. NH_3 soln. (1:1) and diluted to 150 ml. To the soln. obtained by either method add 1 g of Eriochrome black T mixture (1:1000 with NH_4Cl), mix, then run in slowly from a burette 0·2 *M* magnesia mixture till the colour changes to pink, and add 0·5 ml in excess. Mix well, allow to stand for 5 min., filter, wash with a little aq. NH_3 (1:10), and back-titrate the excess of magnesia mixture with 0·1 *M* EDTA to a pure blue end-point. Results for sodium uranate and for process liquors agree satisfactorily whether the phosphate is separated by ion-exchange or pptn. R. E. ESSERY

4063. **Identification of sodium phosphates with an X-ray focusing camera.** D. E. C. Corbridge and F. R. Tromans [Albright and Wilson (Mfg.), Ltd., Oldbury, Birmingham, England]. *Anal. Chem.*, 1958, **30** (6), 1101–1110.—X-ray powder diffraction data, recorded with a Guinier type camera, are presented for 60 crystalline sodium phosphates. Greater resolution and increased definition are obtained than with a Debye - Scherrer type camera and this offers several advantages in the identification and analysis of this class of compound.

K. A. PROCTOR

4064. **Determination of arsenic by means of an extraction method.** Z. Basl, Z. Plašil and R. Štangl (Inst. Res. Ores, Prague). *Rudy*, 1957, **5** (12 Add.), 1–4.—In the rapid method proposed, the sample is decomposed with HNO_3 and H_2SO_4, the As^V is reduced with hydrazine sulphate to As^{III} and extracted in HCl (10·5 to 11 *N*) by shaking with $CHCl_3$. The $CHCl_3$ layer is shaken with water and the As is determined in the aq. layer by iodimetric titration. Only Ge and extremely large amounts of Se interfere. J. ZÝKA

4065. **Successive polarographic determination of arsenic(III and V).** A. H. M. Cosijn and H. J. van der Molen (State Univ., Utrecht, Netherlands). *Anal. Chim. Acta*, 1958, **18** (3), 259–263.—In a soln. containing As^{3+} and As^{5+}, As^{3+} (10^{-3} to 5×10^{-5} *M*) are determined first, after making the soln. *N* with respect to H_2SO_4 and adding 0·01% of gelatin. The polarographic wave for the reduction of As^{3+} occurs at a $E_{\frac{1}{2}}$ of − 0·66 V *vs.* the S.C.E. To a second sample H_2SO_4 is added until its concn. is 80% and the As^{5+} are reduced to As^{3+} by heating at 180° to 200° for 10 min. with hydrazine sulphate (30 mg per ml). The total concn. of As must be 0·028 to 0·0014 *M*. The soln. is then diluted to bring the H_2SO_4 concn. to *N* and the total As is determined polarographically as As^{3+}. The As^{5+} are found by difference.

W. C. JOHNSON

4066. **Determination of arsenic in high-arsenic alloys by means of cationites and complexometric titration.** A. B. Gurevich and V. I. Kalina-Zhikhareva. *Trudy Nauch.-Tekh. Ob. Chernoĭ Metallurg., Ukr. Resp. Pravl.*, 1956, **4**, 127–137; *Ref. Zhur., Khim.*, 1958, Abstr. No. 24,833.—The

method is based on the separation of AsO_4^{3-} from the cations of Fe and other metals with cationites, with subsequent complexometric determination of As, pptd. as NH_4MgAsO_4. Dissolve 0·1 g of iron - arsenic alloy, containing up to 30% of As, in the cold with 50 ml of HNO_3 (1 : 1) and evaporate the soln. almost to dryness. To the residue add HNO_3 (sp. gr. 1·4, 2 ml) and water (20 ml) and heat to complete solution of the salts. Dilute the resulting soln. with cold water to 60 ml and pass it through a column of 60 g of Sulphocarbon or 40 g of KU-2 (H form) at a rate of 10 ml per min. Wash the cationite with water (100 ml) containing 1 ml of conc. HNO_3. From the filtrate precipitate the NH_4MgAsO_4, filter and wash. Subsequent treatment may be carried out in two ways. (*i*) Wash the NH_4MgAsO_4 ppt. from the filter with water, wash the filter with HCl (1 : 1) and water, and make the soln. and wash liquors alkaline to Congo red with aq. NH_3. Add 30 ml of ammoniacal buffer soln. (67 g of NH_4Cl is dissolved in water, 570 ml of 25% aq. NH_3 is added, and the soln. is diluted to 1 litre) and 5 drops of 0·5% acid chrome blue soln. and titrate with 0·05 *N* EDTA (disodium salt) till the wine-red colour changes to lilac - blue. (*ii*) To the soln. obtained after the ion exchange add 40 ml of 0·1 *N* $MgCl_2$ and 15 ml of 25% aq. NH_3, dilute to 250 ml, mix, set aside for 3 hr., and filter off the ppt. on two dense filters. To a 100-ml portion of filtrate add 30 ml of ammoniacal buffer soln. and 5 drops of indicator and titrate with 0·05 *N* EDTA (disodium salt). C. D. KOPKIN

4067. **Determination of arsenic in iron - manganese ores and agglomerates.** N. S. Tkachenko and V. I. Sakunov. *Trudy Nauch.-Tekh. Ob. Chernoĭ Metallurg., Ukr. Resp. Pravl.*, 1956, **4**, 126; *Ref. Zhur., Khim.*, 1958, Abstr. No. 24,832.—Improvement is made in the photometric determination of As as the blue molybdoarsenic complex. Fuse the sample containing $\not>$ 0·3 mg of As with an equal quantity of a mixture (1 : 1) of Na_2CO_3 and ZnO for $\simeq$ 20 min. at 800° to 850°, and cool. Add dil. H_2SO_4 (1 : 4, 10 ml), warm gently, add 1 or 2 g of oxalic acid, heat to decompose oxides of Mn and add KBr soln. [50% (w/v), 2 ml], hydrazine hydrochloride or sulphate (0·5 g) and HCl (sp. gr. 1·19, 20 ml). Distil until the vol. is reduced to 10 ml. Add to the distillate HNO_3 (sp. gr. 1·4, 10 ml), evaporate to dryness, heat the residue for 5 or 10 min. at 170° to 200°, add 90 ml of reagent [1 g of $(NH_4)_2MoO_4$ dissolved in 100 ml of 5 *N* H_2SO_4 (soln. *A*); 0·15 g of hydrazine sulphate dissolved in 100 ml of water (soln. *B*); dilute 10 ml of soln. *A* to 90 ml, add 1 ml of soln. *B* and make up to 100 ml], heat to boiling, cool, dilute with reagent soln. to 100 ml and measure the extinction with a red filter. C. D. KOPKIN

4068. **Gallein as a reagent for colorimetric determination of antimony(III).** Shu-Wei Pang and Ming-Lein Lu. *Acta Chim. Sinica*, 1957, **23** (2), 117–123.—Gallein is used for quant. determinations, a compound being formed which is only slightly soluble in water and is insoluble in many organic solvents. The accuracy is $\pm$ 0·55% and the degree of interference shown by Ba, Pb, Fe, Sn and Cl is indicated. S.C.I. ABSTR.

4069. **A new method of determination of antimony in copper alloys.** E. Mohr (VEB Berlin, Metallhütten- u. Halbzeugwerke). *Chem. Tech., Berlin*, 1958, **10** (1), 34–35.—A procedure for determining Sb in copper alloys involves dissolving the alloy (3 g) in H_2SO_4 - HNO_3 - H_2O (2 : 1 : 5, by vol.) (30 ml) heating to expel nitrous gases and adding formic acid (5 ml). The soln. is then evaporated to incipient crystallisation of the copper salt. After the addition of water (100 ml) and conc. HCl (10 ml), aq. NH_3 is added until the soln. is deep blue. The ppt. is washed with hot water, filtered off and dissolved in dil. HCl (1 : 1) (15 ml); $MnSO_4$ soln. (20% w/v in 40% v/v H_2SO_4) (10 ml) is added and the soln. is titrated with $KMnO_4$ in the cold. The method can be used for gun metal, bronze and brass. For brass, 7 g is used and more acid solvent in proportion. After the titration with $KMnO_4$, Sn may be determined in the soln. C. A. FINCH

4070. **Determination of traces of metals by the extraction of inorganic compounds with organic solvents. I. Determination of vanadium.** Hidehiro Gotô and Shigero Ikeda (Inst. of Iron, Steel and other Metals, Tohoku Univ., Katabiracho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (2), 152–155.—The thiocyanate complex of VIII (Crouthamel *et al.*, *Anal. Chem.*, 1955, **27**, 507) is extractable from an acid soln. ($\simeq$ *N* HCl) into an org. solvent such as ethyl acetate, butyl acetate, amyl acetate, *iso*propyl alcohol or *iso*butyl alcohol. The absorption spectrum and the molar extinction coeff. are almost identical in these solvents. The working curve is linear for $<$ 100 μg per 10 ml. The sample soln. containing VO_3^- is mixed with $SnCl_2$ soln. (20% in *N* HCl) (2 ml), KSCN soln. (20%, 2 ml) and dil. HCl to produce $\simeq$ 10 ml of *N* HCl soln. The product is shaken with the solvent (10 ml) for 1 min. and the extinction measured at 396 mμ. Titanium, Co, Mo and Fe interfere. K. SAITO

4071. **New volumetric method for the determination of vanadium in triheteropoly acids.** A. I. Kokorin and M. S. Shchelkunova. *Uch. Zap. Kishinevsk. Univ.*, 1957, **27**, 79–82; *Ref. Zhur., Khim.*, 1958, Abstr. No. 14,173.—This method for determining V in molybdovanadium and tungstovanadium heteropoly acids of P and Si is based on the titration of V with a soln. of Ti^{3+}, with a mixture of Na_2MoO_4 and H_3PO_4 as indicator. Dissolve the sample ($\simeq$ 2 g) in 50 ml of water, add solid NaOH to a 5-ml aliquot, boil till the soln. is colourless, cool, add H_2SO_4 (1 : 1) (5 ml), 0·1 *N* $Na_2MoO_4.2H_2O$ (5 ml) and conc. H_3PO_4 (1 or 2 ml), and titrate with 0·05 *N* $TiCl_3$ in 4 *N* H_2SO_4 to a dark-green colour, which changes to blue after several seconds. The method has the advantages that no phenylanthranilic acid is required, and the colour change at the end-point is satisfactorily sharp. C. D. KOPKIN

4072. **Rapid method for the separation of tantalum from niobium and of the mixed oxides from zirconia.** B. S. Krishna Rao, D. V. N. Sarma and B. S. V. Raghava Rao (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1958, **160** (5), 351–353 (in English).—The morin complexes of Ta and Nb are pptd. together by adding H_2SO_4 (25 ml) in the cold followed by morin (1·5 g in 30 ml of ethanol), at 50°, to 75 ml of sample soln. (up to 0·05 g of each oxide in 10% oxalic acid) and boiling. After 3 hr. the niobium complex is dissolved by the addition of 15% H_2SO_4 in acetone (200 ml) and the soln. is filtered. The ppt. is washed with 25% H_2SO_4 in

acetone (30 to 40 ml) and then with H_2SO_4 (6 ml) in ethanol (30 ml), ignited and weighed as Ta_2O_5. If less Nb than Ta is present in the sample, Ta is quant. separated from Nb and Zr. G. BURGER

4073. **Photometric determination of tantalum in the presence of titanium.** C. E. Gracias. *Técnica, Lisbon*, 1957, **31** (271), 433–439; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,560.—The colour reaction of Ta with pyrogallol (**I**) can be used for the photometric determination of Ta even in the presence of large amounts (up to 60%) of Ti. In acid medium Nb causes practically no interference. Prepare a soln. from the mineral and separate a mixture of Ta_2O_5, Nb_2O_5 and TiO_2. Fuse 0·1 g of the mixed oxides in a quartz crucible with 5 g of $K_2S_2O_7$, extract the melt with a saturated ammonium oxalate soln. and make up to 100 ml. To a 5-ml aliquot add $K_2S_2O_7$ (7 g), **I** (10 g) and saturated ammonium oxalate soln. (60 g), make up to 100 ml and measure the extinction of the soln. at 400 mμ (total extinction of the complexes of Ta and Ti with **I**, $A_{Ta} + A_{Ti}$). To another 5-ml aliquot add H_2SO_4 (1:1) (10 ml), 3% H_2O_2 soln. (10 ml) and saturated ammonium oxalate soln. (40 ml), make up to 100 ml and measure the extinction at 435 mμ (the peroxide complex of Ti, A). From A is found the quantity of Ti, which from a calibration curve gives the amount of the complex of Ti with **I**, A_{Ti}. This is subtracted from $A_{Ta} + A_{Ti}$ and the amount of Ta is found from A_{Ta}. The error is < 1%. C. D. KOPKIN

4074. **Titration of hydrogen sulphide and sulphides with organomercury compounds.** M. Wroński and B. Philipp (Ger. Acad. Sci., Berlin). *Faserforsch. u. Textiltech.*, 1958, **9** (1), 36–37.—Reliable works control methods are developed for estimating H_2S and sulphides in liquors and in air or waste gases in the cellulose and viscose industries by titration with soln. of hydroxymercuribenzoic acid (**I**). The titrations are not affected by even large amounts of iodine, sulphite, SCN^- or Cl^-, but CN^- should be absent. For estimating dissolved sulphides (including polysulphides), the sample liquor (of suitable size and dilution) is titrated to a sharp end-point (normally colourless from deep blue or bluish shade) with a 0·05 *N* soln. of **I** (prepared by dissolving 16 g of **I** in 100 ml of *N* NaOH, and diluting to 1 litre, and standardised against 0·1 *N* soln. of sulphide in aq. NaOH); the indicator is a 0·5% soln. in 0·1 *N* NaOH of thiofluorescein (**II**) titrated till colourless with 0·05 *N* **I**. To estimate H_2S in air or other gas, the gas is drawn in metered amount through a measured vol. of a soln. of known H_2S equivalency, prepared by titrating the 5% soln. of **II** with diluted 0·05 *N* **I**, the amount of gas necessary to give a blue coloration serving to fix the H_2S content. The presence of CO_2, SO_2 or SO_3 in the gas does not affect the results, nor do amounts of CS_2 < 10% of the saturation pressure; COS reacts as sulphide and is so estimated. H. L. WHITEHEAD

4075. **Analysis of concentrated sulphur-containing gases.** K. E. Perepelkin and Ya. Z. Sorokin. *Zavod. Lab.*, 1957, **23** (12), 1414–1417.—To analyse mixtures of H_2S, CS_2 and COS, the sample is first passed through an acid soln. of zinc or cadmium acetate and the pptd. sulphide is determined iodimetrically. A small amount of CS_2 and a smaller amount of COS are absorbed, but are removed by passage of air through the soln. The gas is then passed through ethanolic NaOH soln. followed by iodimetric determination of the xanthates to give the sum of CS_2 and COS. From a determination of the total content of S in the original gas, by burning it with air to give SO_2, which is absorbed in neutral H_2O_2 soln. and then titrated with alkali, the contents of the individual gases can be found. G. S. SMITH

4076. **Coulometric titrations with mercury(I) and (II). Determination of sulphide.** E. P. Przybylowicz and L. B. Rogers (Dept. of Chem., M. I. T., Cambridge, Mass., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1064–1069.—The solubility product of HgS is very low and is the basis for a sensitive coulometric titration procedure for very small amounts of S^{2-}. The titration is made potentiometrically at 80° (to minimise adsorption) with Hg generated at ≃ 100% efficiency in 0·1 *M* NaOH with mercury-coated electrodes in the apparatus described previously (*cf. Anal. Abstr.*, 1956, **3**, 3043). The generating current is ≃ 10 mA and the end-point is at ≃ − 0·5 V *vs.* the S.C.E. With 100 ml of soln., from 0·24 to 1·1 mg of S^{2-} can be determined to within ≃ ± 0·2%, and amounts down to 0·06 mg with an increasing error up to 2%. Factors influencing the accuracy and limiting the use of the method are discussed. W. J. BAKER

4077. **Paper chromatography of sulphuric acid, its salts and derivatives.** H. A. Lehmann and G. Kempe (Tech. Hochschule für Chemie, Leuna-Merseburg). *Chem. Tech., Berlin*, 1957, **9** (12), 719–720.—Soln. of sulphur compounds are chromatographed on paper and treated with N_2O_3 (if S other than SO_4^{2-} is known to be present) to remove interfering ions and convert other sulphur compounds into SO_4^{2-}, which are detected by conversion into PbS with $Pb(NO_3)_2$ and alkaline Na_2S soln. The chromatogram, after drying, is exposed for 2 hr. to N_2O_3, then heated to 100°, and sprayed with 1 ml of $Pb(NO_3)_2$ soln., and excess of Pb is removed by immersion in saturated $PbSO_4$ soln. The paper is washed and finally sprayed with a soln. of 2% Na_2S - 2% NaOH. About 4 mg of S can be detected. The method was applied to (*a*) a mixture of sulphate, imidosulphate, sulphamate, iminodisulphamide and sulphamide in dioxan - H_2O - 25% aq. NH_3 (75:24:1), and gave R_F values of 0·05, 0·18, 0·36, 0·52 and 0·84, respectively; (*b*) a mixture of alkali and ammonium sulphates in *iso*propyl alcohol - ethanol - water (3:4:3), and gave R_F values for Li of 0·59, NH_4^+ 0·44, Na 0·33, K 0·21, Rb 0·21 and Cs 0·21; (*c*) mixtures of polythionates in *iso*propyl alcohol - ethanol - water. J. L. PROSSER

4078. **Complexometric determination of sulphate.** K. F. Sporek (Eldorado Mining and Refining, Ltd., Ottawa, Canada). *Anal. Chem.*, 1958, **30** (6), 1032–1035.—The amount of SO_4^{2-} in materials from the extraction of uranium ores can be determined, in ≃ 40 min., by pptn. as $PbSO_4$. The sample (≯ 3 g) is dissolved in a boiling mixture of conc. HNO_3 and HBr, and after addition of water and *iso*propyl alcohol, and filtration, 10% (v/v) HNO_3, 50% (v/v) *iso*propyl alcohol and a 0·05 *M* excess of $Pb(NO_3)_2$ are added to the filtrate. The ppt. is collected and dissolved in a 0·1 *M* soln. of EDTA (disodium salt), and the excess of EDTA is then back-titrated with 0·05 *M* $ZnCl_2$, with Eriochrome black T as indicator. The procedure given is virtually free from interference by PO_4^{3-}, AsO_4^{3-}, Fe and U and has approx. the same accuracy as the gravimetric method. W. J. BAKER

4079. **Spectrophotometric determination of small amounts of sulphate ions. I. Use of solid barium chromate or a hydrochloric acid solution of barium chromate.** Iwaji Iwasaki, Satori Utsumi, Ken Hagino, Toshikazu Tarutani and Takejiro Ozawa (Tokyo Inst. of Tech., Ookayama). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (1), 32–38.—The optimum conditions for the pptn. of SO_4^{2-} with a suspension of $BaCrO_4$ (*Ibid.*, 1953, **74**, 400) are a pH of 6·5, an ethanol concn. of 10% v/v, and 60 mg of $BaCrO_4$ for 0·2 to 12 p.p.m. of SO_4^{2-}. The $BaCrO_4$ must be pptd. from an HCl soln. with aq. NH_3. After being shaken for 3 min., the CrO_4^{2-} are determined colorimetrically with diphenylcarbazide (**I**) (1% in ethanol) in 6 *N* HCl soln. (0·2 ml) at 545 mμ. For > 20 p.p.m. of SO_4^{2-} (sample 5 ml), an HCl - acetic acid soln. of $BaCrO_4$ (0·2 g in 0·1 *N* HCl containing 0·5 *N* acetic acid) (1 ml) can be used, followed by the pptn. of $BaCrO_4$ with 6 *N* aq. NH_3 soln. containing 1 mg of Ca^{2+} per ml, in the presence of ethanol (1 + 1, by vol.). The use of Ca^{2+} prevents the adsorption of CrO_4^{2-} on $BaCrO_4$.

II. Use of barium chromate suspension in an acid solution. Iwaji Iwasaki, Ken Hagino and Satori Utsumi. *Ibid.*, 1958, **79** (1), 38–44.—The use of a suspension of $BaCrO_4$ (2·5 g in 0·5 *N* acetic acid containing 0·1 *N* HCl) (Iwasaki *et al.*, *Bull. Chem. Soc. Japan*, 1957, **30**, 847) is superior to that reported in Part I, for 0·3 to 100 p.p.m. of SO_4^{2-}. Interference results from AsO_4^{3-}, PO_4^{3-}, VO_3^-, SeO_4^{2-}, Pb, Cu (> 10 p.p.m. each) and a large amount of NO_3^- (1000 p.p.m.), K (2000 p.p.m.) and NH_4^+ (2000 p.p.m.). *Procedure*—Mix the sample (5 ml) with the reagent (2 ml), then, after a few minutes, with 6 *N* aq. NH_3 soln. containing 1 mg of Ca per ml (0·5 ml) and ethanol (5 ml). Centrifuge after 10 min. and measure the extinction of the soln. at 370 mμ, or mix with **I** soln. (0·1% in ethanol) (1 ml) and 6 *N* HCl (0·7 ml) and measure at 545 mμ after 5 min.

III. Colorimetric determination of a trace of sulphate ions (0·02 to 5 p.p.m.) in natural water. Iwaji Iwasaki, Satori Utsumi, Ken Hagino and Takejiro Ozawa. *Ibid.*, 1958, **79** (1), 44–50.—The amount of CrO_4^{2-} passing from $BaCrO_4$ into the aq. layer depends on the concn. of SO_4^{2-}, the rate remaining constant for a given amount of SO_4^{2-}, $BaCrO_4$ and ethanol at a given pH. This principle is applied to the determination of a very small amount of SO_4^{2-}. *Procedure*—Mix the sample (10 ml) with an acetate buffer (2 *M*) (0·5 ml) of pH 3·6 and ethanol (3 ml). Keep in a thermostat (20°) for a few minutes, add $BaCrO_4$ (50 mg), shake for 3 min. and centrifuge. Treat the supernatant soln. (filtered through a sintered glass filter) with **I** soln. (1 ml) and 6 *N* HCl (0·2 ml) and measure the extinction at 545 mμ after 5 min. K. Saito

4080. **Potentiometric determination of water-soluble sulphates.** D. E. Galkin. *Trudy Tomsk. Univ.*, 1957, **145**, 69–72; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,590.—The method described for the rapid determination of SO_4^{2-} in mixtures of H_2SO_4 and HNO_3, in water-soluble mixtures of sulphates and nitrates, and in mirabilite and thenardite, is based on the potentiometric titration of SO_4^{2-}, with a bimetallic system of electrodes (platinum and silver). To the soln. to be analysed add 0·005 *M* $K_4Fe(CN)_6$ (0·1 ml) and 0·1 *M* $K_3Fe(CN)_6$ (1 ml), dilute with an equal vol. of 96% ethanol and titrate with $Pb(NO_3)_2$ soln. to the max. deviation of the needle of a galvanometer connected with the electrodes and with a resistance of 30,000 to 50,000 ohms. The error of the determination is ±0·14% (abs.). C. D. Kopkin

4081. **Interpretation of some anomalies in the determination of sulphate ions by indirect flame photometry.** F. Burriel-Martí, J. Ramírez-Muñoz and M. L. Rexach-M. de Lizarduy (Fac. de Ciencias, Univ., Madrid). *Rev. Cienc. Apl.*, 1958, **12** (60), 16–25.—The effects of concentration, adsorption and the presence of other salts in the determination of SO_4^{2-} by photometric measurement of the decrease in the concn. of the "basic element" (Ba or Sr) are examined. The deviations of the experimental curves from the theoretical straight line in a Ba *vs.* SO_4^{2-} graph caused by the influence of the solubility product of $BaSO_4$, by adsorption of the cations on the ppt., and by the addition of KNO_3, KI, KBr, NaCl, KCl and borax in high concn. are interpreted. It is concluded that it is necessary to use experimental curves obtained from soln. with known SO_4^{2-} concn. and a composition similar to that of the analysed soln., or to determine previously the variations of the apparent concn. of the "basic element" as a function of the concn. and nature of the additional salts. In any case, the use of Ba as the "basic element" gives more reliable results. H. Friedmann

4082. **Analytical determination of selenium and tellurium in ores and their decomposition products.** M. F. Proshkovich and P. V. Faleev. *Obogashchenie Rud*, 1957, (2), 21–24; *Ref. Zhur., Khim.*, 1958, Abstr. No. 14,205.—Methods are described for the decomposition of large samples (low-grade ores, flotation tailings of copper - nickel ores and slags) without losses of Se and Te, with a mixture of HNO_3 and H_2SO_4 or a mixture of aqua regia and H_2SO_4. The latter mixture is preferable if the sample contains Ag which, in the absence of Cl^-, forms the difficultly soluble $AgTeO_3$. To remove HNO_3, evaporate the soln. to the crystallisation point, and destroy the remaining HNO_3 by the addition of formaldehyde. To dissolve the material with simultaneous separation of Se as the volatile $SeBr_4$, heating with a mixture of Br and HBr is recommended. Separate Se and Te from platinum metals as $Fe_2(SeO_3)_3$ and $Fe_2(TeO_3)_3$ in the presence of $NaNO_2$ at low acidity (pH 5·2), produced by the addition of an aq. suspension of ZnO. Comparative results are given for the separation of Se and Te from platinum metals by other methods—(*i*) pptn. with hydrazine in H_2SO_4 soln., (*ii*) dissolution of Se and Te in $(NH_4)_2S$ soln., with subsequent separation of Te by warming with Na_2SO_3, (*iii*) pptn. of Te as $Fe_2(TeO_3)_3$ in weakly ammoniacal medium, and (*iv*) pptn. of Te as $Fe_2(TeO_3)_3$ by hydrolysis of the acetates in weakly acid medium. Methods (*i*) and (*ii*) do not ensure complete separation of Te from the platinum metals, and methods (*iii*) and (*iv*) do not ensure favourable determination of Se. For the separation of Se and Te, the most useful method is to use a soln. of hydrazine in 28% HCl. For the determination of Se and Te, it is recommended to use photometry of their colloidal soln., obtained by reduction with $SnCl_2$, or iodimetric titration. C. D. Kopkin

4083. **Determination of small amounts of arsenic in selenium.** J. F. Reed (Westinghouse Res. Lab., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1122–1124.—As little as 2 μg of As in rectifier-grade selenium (2-g sample) can be determined accurately by an initial quant. pptn. of Se with

SO_2 (Hillebrand *et al.*, "Applied Inorganic Analysis," Wiley, N.Y., 1953, p. 259), followed by complexing the As in the filtrate with molybdate - hydrazine reagent and measurement of the extinction of the molybdenum-blue complex at 808 mμ against a reagent blank. Phosphorus and some oxidising agents, *e.g.*, Fe^{3+}, interfere. For ≃ 20 p.p.m. of As the standard deviation is 1·2 p.p.m. (6 analyses).
W. J. BAKER

4084. **Determination of tervalent chromium in the presence of chromate.** R. W. Cline, R. E. Simmons and W. R. Rossmassler (Union Carbide Nuclear Co., Paducah Plant, Ky., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1117–1118.—From 0 to 0·5 p.p.m. of Cr^{3+} in H_2O containing ≃ 300 p.p.m. of chromate can be determined by a double pptn. of $Cr(OH)_3$, with $Al(OH)_3$ as carrier. The ppt. is dissolved in H_2SO_4, and the Cr^{3+} in an aliquot of the diluted soln. are oxidised to chromate with bromine water. After removing the excess of Br with phenol and adding 1 ml of diphenylcarbazide reagent, the Cr is determined spectrophotometrically at 540 mμ (slit width 0·03 mm) against a water blank. The chromate in an unoxidised aliquot should also be determined although it rarely exceeds 0·03 p.p.m. The content of Cr^{3+} in the sample is obtained by reference to a standard curve. Reproducibility is good and recovery of Cr is complete.
W. J. BAKER

4085. **Photometric determination of chromium in ferro-alloys with diphenylcarbazide.** Takuya Imai and Shinko Nagumo (Nippon Denko Co., Shinagawa-ku, Tokyo). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1958, **61** (1), 53–55.—There is no interference from Fe, Mo, Cu, Ni and V in the photometric determination of Cr (540 mμ) with diphenylcarbazide (**I**). To avoid the effect of a large amount of Mn, oxidation with $(NH_4)_2S_2O_8$ is recommended. The time taken for a determination is ≃ 20 min. *Procedure*—Dissolve ferromanganese (0·2 g) in HNO_3 (5 ml), H_2SO_4 (1 + 1, 6 ml) and water (40 ml), add H_3PO_4 (2 ml), $AgNO_3$ soln. (0·5%, 5 ml) and $(NH_4)_2S_2O_8$ soln. (10%, 2 ml) and boil for 4 min. after the violet colour of $KMnO_4$ has appeared. Add urea soln. (10%, 20 ml) and $NaNO_2$ soln. (10%) until the colour is discharged, and dilute to 250 ml. Make up a 50-ml portion to 100 ml with **I** (0·2% in 95% ethanol, 3 ml) and HF (4%, 5 ml). Dissolve ferrosilicon and silicomanganese in HNO_3 (2 ml), HF (40%, 2 ml) and H_2SO_4 (1 + 1, 6 ml), and ferromolybdenum in HNO_3 (7·5 ml), HCl (2·5 ml) and H_2SO_4 (1 + 1, 6 ml).
K. SAITO

4086. **Volumetric determination of molybdenum.** R. Weiner and P. Boriss (Univ. Innsbruck, Austria). *Z. anal. Chem.*, 1958, **160** (5), 343–351.—By means of a silver reductor, Mo^{6+} are reduced to Mo^{5+}, which are stable in air and can be titrated with $K_2Cr_2O_7$ in the presence of H_3PO_4 with diphenylamine as indicator. The reductor comprises a tube 2 cm in diam. filled to a height of 12 cm with silver powder. The lower end is fitted with a stop-cock, and the upper end with a tap-funnel. Before use it is conditioned by the passage of 100 ml of 2 *N* HCl. The sample, which should contain 200 to 300 mg of MoO_3 in 2 *N* HCl (50 ml), is passed through the reductor at a rate of 5 to 10 ml per min. The reductor is then washed with 2 *N* HCl (100 ml). The $K_2Cr_2O_7$ soln. should be standardised against MoO_3 treated in the same manner. The scatter of 8 results lies within the limits of precision of volumetric analysis. When an error of 1% is permissible, Mo^{6+} can be titrated potentiometrically with $AgNO_3$ in acetate buffer soln. Addition of ethanol sharpens the end-point.
G. BURGER

4087. **Potentiometric titration of molybdenum by means of silver nitrate solution.** B. Valgand. *Glasnik Zem. Drushtva*, 1957, **22** (1), 51–54; *Ref. Zhur., Khim.*, 1958, Abstr. No. 35,911.—The investigation of the application of the potentiometric titration of MoO_4^{2-} by means of $AgNO_3$ soln. at pH 5 to 10 in H_2O - ethanol (1:1 and 1:2) has been described. This titration is possible in a limited pH range of 7 to 8·5. The presence of ammonia or ammonium salts forming a $[Ag(NH_3)_2]$ complex causes interference with the titration; for the determination of MoO_4^{2-} in ammonium molybdate soln., the latter must be converted into sodium molybdate by the addition of NaOH. The presence in 40 ml of the titrated soln. (≃ 0·05 *M*) of 1 g of Na_2SO_4, K_2SO_4, $NaNO_3$, KNO_3 or Na acetate does not cause interference. When titrating 100 ml of 0·0025 *M* sodium molybdate soln. in 50% ethanol with 0·1 *N* $AgNO_3$ the error was ± 1·4%.
W. ROUBO

4088. **Estimation of molybdenum and rhenium in Indian columbite.** Sujata Sen (Univ. Coll. Sci., Calcutta). *Sci. & Cult.*, 1957, **23** (6), 318–319.—Molybdenum is pptd. as sulphide which is converted into molybdate by NaOH and H_2O_2. This is then treated with $SnCl_2$ and SCN^- and the complex is extracted with ether; the Mo is determined spectrophotometrically by comparison with a standard curve. For Re, the ore is fused with Na_2O_2. After adjustment of the pH and Cl^- concn., the ReO_4^- are separated from molybdate by tetraphenylarsonium chloride and extraction with $CHCl_3$ (Trilabat, *Anal. Chim. Acta*, 1949, **3**, 113). The $CHCl_3$ soln. after drying is treated with $SnCl_2$ and SCN^- and the concn. of Re is determined spectrophotometrically in $CHCl_3$ - amyl alcohol by comparing with a standard.
N. E.

4089. **Determination of molybdenum and tungsten. XI. 4-Amino-4′-chlorodiphenyl as precipitant.** Shu-Chuan Liang and Shun-Jung Wang (Inst. of Chem., Acad. Sinica, Peking). *Acta Chim. Sinica*, 1958, **24** (1), 117–121.—4-Amino-4′-chlorodiphenyl (**I**) (*cf.* Belcher *et al.*, *Brit. Abstr. C*, 1953, 422) has been used in the gravimetric determination of W^{VI} and Mo^{VI}. Variables in the test are examined, such as acidity and temp. for pptn., amount of precipitant, temp. for ignition and interference by some alkali metals. For the determination of W, add 100 ml of **I** soln. (0·03% in 0·02 *N* HCl) to the sample soln. containing up to 75 mg of W. Adjust to a pH of 1·5 to 3·1, and heat at almost boiling-point on a hot-plate for 2 hr. Cool to about 60°, then filter. Ignite the residue at 625° to 850° until the wt. is constant, and weigh as WO_3. The presence of NH_4Cl (2 g), $NaNO_3$ (2·5 g) and ammonium acetate (2 g) causes no significant effect, but NaCl or KCl (2·5 g) causes positive error. A similar procedure is used for the determination of Mo, but pptn. is carried out at pH 1·8 to 2·8 and ignition at 550°.
S. H. YUEN

4090. **Colorimetric determination of molybdenum in the presence of tungsten. Modified mercaptoacetate method.** D. A. Otterson and J. W. Graab (Lewis Flight Propulsion Lab., Nat. Advisory Committee for Aeronautics, Cleveland, Ohio).

Anal. Chem., 1958, **30** (7), 1282–1284.—The method of Will and Yoe (*Anal. Chem.*, 1953, **25**, 1363) has been modified to eliminate interference by W. The alloy sample is dissolved in acid, and the Mo and other metals, including W, are pptd. by benzoin α-oxime soln. This ppt. is dissolved in a small vol. of 5% NaOH soln. and diluted to a known vol. A 2·5% soln. of citric acid is added to an aliquot of this alkaline soln. and the pH adjusted to 4. A soln. of ammonium mercaptoacetate is then added and the colour produced is measured at 365 mμ. In the presence of up to 60% of W, the Mo in samples of alloy can be determined with an error of ≃ 1%. Three other components of high-temp. alloys, namely Nb, Ta and Zr, do not interfere in moderate amounts, but only traces of Ti can be tolerated. G. S. ROBERTS

4091. **Detection of uranium(VI) by salicylaldoxime.** G. Almássy (Res. Inst. for Physics, Acad. Sci., Debrecen, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **15** (3), 225–229 (in English).—*Cf. Magyar Kém. Foly.*, 1955, **61**, 404 (in Hungarian); *Anal. Abstr.*, 1956, **3**, 1705. T. R. ANDREW

4092. **Determination of traces of uranium with 1-(2-pyridylazo)-2-naphthol.** K. L. Cheng (Westinghouse Electric Corp., East Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1027–1030.—Trace amounts of U in the presence of many metals can be determined without initial separation by addition to the soln., containing EDTA and nitrilotriacetic acid (or KCN) and buffered to pH 10, of a few ml of a 0·1% soln. of 1-(2-pyridylazo)-2-naphthol (PAN) in methanol. The naphthol complex (a deep-red finely divided ppt.) is extracted with *o*-dichlorobenzene and its extinction is measured at 570 mμ. The colour is stable and Beer's law is valid from 0·1 to 5 × 10^{-4} millimole of U in 10 ml of the solvent. The molar absorptivity of the complex is 2·3 × 10^4, so that the sensitivity of the method is very high. Phosphates and iodine interfere, and H_2O_2 inhibits the reaction. W. J. BAKER

4093. **Determination of uranium using disodium 1:8-dihydroxynaphthalene-3:6-disulphonate (chromotropic salt) as a colorimetric reagent.** Anil K. Mukherji and Arun K. Dey (Chem. Lab., Univ. of Allahabad). *J. Indian Chem. Soc.*, 1958, **35** (2), 113–118.—The use of this reagent for the determination of U on a micro scale is described. The reagent is sensitive to 30 p.p.m. of U and Beer's law is obeyed in the range 50 to 200 p.p.m. The molar concn. of the reagent should be ≮ 30 times that of U and the pH of the medium should be adjusted to 4·00 ± 0·50. Either a photoelectric colorimeter with a blue filter or a spectrophotometer can be used. The molar ratio of the components in the chelate is 1:1. The interference of various cations and anions is discussed.
I. JONES

4094. **New method for the determination of very small amounts of uranium and its application to the analysis of stone meteorites.** K. H. Ebert, H. König and H. Wänke (Max Planck Inst. f. Chemie, Mainz, Germany). *Z. Naturf.*, 1957, **12a** (10), 763–765.—When uranium is irradiated by a neutron beam, ^{133}Xe is produced to the extent of 6·5% of the uranium present in the sample. This xenon with a half-life of 5·27 days is separated and its activity measured. Traces of atmospheric xenon are removed from the sample before irradiation by heating the sample for several hours at 400° in a high vacuum. Inactive carrier xenon is used to drive the active xenon out of the material, and the total gas after removal of oxygen and nitrogen is adsorbed on carbon, of which the activity is counted over a period of several weeks. From the resulting decay curve a half-life of 5·27 days exactly was obtained, which confirms the absence of other fission products. Analysis shows that 10^{-9} g of U may be determined by this method. Results for three chondrites are presented.
E. KAWERAU

4095. **Polarography of uranium in phosphoric acid.** Tê-Yao Ch'i. *Acta Chim. Sinica*, 1957, **23** (2), 79–89.—Uranium in moderate concn. in H_3PO_4 soln. produces two distinct waves, these being identified as corresponding to the reactions involving U^V and U^{IV}; the characteristics of these waves have been analysed. A method for the simultaneous determination of U^{IV} and U^{VI} is proposed and the work carried out indicates that it has practical application. S.C.I. ABSTR.

4096. **Coulometric titration of uranium and uranium - vanadium mixtures with titanium(III).** J. H. Kennedy and J. J. Lingane (Harvard Univ., Cambridge, Mass., U.S.A.). *Anal. Chim. Acta*, 1958, **18** (3), 240–244.—Sexavalent U (8 to 225 mg) is titrated coulometrically with Ti^{3+} electrogenerated by reduction of Ti^{4+} at a platinum electrode. The supporting electrolyte (100 ml) is 0·6 *F* titanyl sulphate in 8 *F* H_2SO_4 and contains Fe^{2+} (0·0002 to 0·0003 *M*) to serve as a catalyst for the second reaction stage $U^{5+} + Ti^{3+} \rightarrow U^{4+} + Ti^{4+}$. Amperometric end-point detection is used. A similar procedure is used for the determination of V^{5+} and U^{6+} in the same soln. An end-point is obtained for the reduction of V^{5+} to V^{4+}, the Fe^{2+} catalyst is then added and the second part of the titration consists in the simultaneous reduction of V^{4+} to V^{3+} and of U^{6+} to U^{4+}. W. C. JOHNSON

4097. **Radiometric methods for the determination of uranium and thorium in minerals.** D. Prosperi and S. Sciuti (Com. Naz. Ric. Nucleari, Italy). *Ric. Sci.*, 1958, **28** (2), 345–361.—After a critical review of existing methods, a procedure is proposed for the determination of U and Th in minerals, where the activities from the two series are comparable and the former is out of equilibrium. A γ-γ-β method is used which involves simultaneous measurement of β-activity and of γ-activity at two different energy levels. Samples containing > 0·02% of U may be analysed and the two families distinguished when U to Th ≮ 0·03, even when the U family is not in equilibrium.
L. A. O'NEILL

4098. **Complex formation of uranyl ion with *o*-cresotic [2-hydroxy-*m*-toluic] acid: potentiometric, colorimetric and conductimetric study.** S. C. Tripathi and Satya Prakash (Chem. Lab., Univ. of Allahabad). *J. Indian Chem. Soc.*, 1958, **35** (2), 119–124.—The formation of a red complex containing uranyl and 2-hydroxy-*m*-toluate in 1:1 molar ratio at ≃ pH 4·5 is shown by the inflection, break and maximum in colorimeter reading at one equivalent of alkali in all the potentiometric, conductimetric and colorimetric titration curves of different mixtures of uranyl nitrate and sodium 2-hydroxy-*m*-toluate. I. JONES

4099. **Separation of uranium [uranyl] from other metals in sulphate solution by fractional hydrolysis. I. Hydrolysis in sulphate solution.** T. V. Arden and J. Harbutt (Chem. Res. Lab., Teddington, Middx., England). *J. Appl. Chem.*, 1958, **8** (3), 141–150.—Uranium may be pptd. from an UO_2SO_4 soln. at pH 4·0 to 6·2 with NaOH or $Ca(OH)_2$ soln., the product being $U_3O_8(OH)_2$. Separation from Fe^{3+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Ca^{2+} and Mg^{2+} can be achieved by controlled addition of the alkali, but separation from Al^{3+} and Cu^{2+} is not complete. Curves of pH *vs.* vol. of titrant for various cation soln. with NaOH and $Ca(OH)_2$ are presented.

II. Precipitation in the presence of phosphate, arsenate and silicate. T. V. Arden, R. Humphries and J. A. Lewis. *Ibid.*, 1958, **8** (3), 151–159.—Similar pH - titrant curves are presented for several cations with NaOH soln. in the presence of PO_4^{3-}, AsO_4^{3-} and SiO_3^{2-}. It is concluded that by hydrolytic pptn., separation of UO_2^{2+} from Fe^{3+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+} and Cu^{2+}, but probably not from Al^{3+}, can be achieved in the presence of PO_4^{3-} at pH 1·9 to 2·5, and from the same ions, except Fe^{3+} but including Al^{3+}, in the presence of AsO_4^{3-} at pH 1·3 to 1·7; pptn. in the presence of SiO_3^{2-} is less selective. Several separation schemes for UO_2^{2+} are presented.

D. A. PANTONY

4100. **Radiochemical determination of ionium in uranium fluorination ash.** F. L. Moore (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1020–1021.—The carrier-free radiochemical method described gives an average yield of 97 ± 3% and may be applied in the presence of other alpha emitters. A combination of lanthanum hydroxide and fluoride pptn. carries down the ionium quant.; it is then extracted selectively with 2-thenoyltrifluoroacetone - xylene. The activity is measured in a proportional alpha counter.

K. A. PROCTOR

4101. **Separate determination of natural radioactive elements by the use of laboratory radiometric methods.** I. M. Nazarov. *Atomnaya Energiya*, 1957, **3** (8), 121–129; *Ref. Zhur., Khim.*, 1958, Abstr. No. 28,396.—Descriptions are given for the separate radiometric determination of natural radioactive elements in rocks, ores, minerals, etc., based on (*i*) measurement of the various types of radiation (α, β, γ); (*ii*) discrimination of the radiation of one type; (*iii*) the use, in addition to measurements of one type, of supplementary emanation measurements; (*iv*) combination of measurements of types (*i*) and (*ii*). General equations are given for the separate determination of radioactive elements, including U, Ra and Th. The accuracy of the determinations is discussed.

C. D. KOPKIN

4102. **Improvements in the determination of fluorine in products of zinc and lead production.** L. N. Krasil'nikova and S. M. Milaev. *Sb. Trud. Vses. Nauch. Inst. Tsvet. Met.*, 1956, (1), 169–171; *Ref. Zhur., Khim.*, 1958, Abstr. No. 21,193.—It is established that, as a result of preliminary ignition of the products to be analysed, at 800°, part of the F is volatilised, so that in the subsequent determination of F incorrect results are obtained. To oxidise sulphide S, fusion with Na_2O_2 is used, instead of the ignition. Fuse 0·5 to 1 g of sample with 5 or 6 g of Na_2O_2 in an iron crucible at 550° to 600°, extract the melt with water, neutralise the soln. with H_2SO_4 and add sufficient acid to give a 50% H_2SO_4 soln. Distil off HF, make the distillate alkaline with NaOH soln., evaporate to 20 or 30 ml and then make up to 50 or 100 ml. To an aliquot of the soln. (containing 0·1 to 0·2 mg of F) in a colorimetric cylinder add 5 ml of a peroxide - titanium sulphate soln. (0·1 mg of Ti per ml) and determine F by the change in colour. Reproducible results were obtained in the determination of F in zinc concentrate, lead dust, zinc oxide, zinc dust and zinc cake.

C. D. KOPKIN

4103. **Rapid estimation of hydrofluoric acid in red fuming nitric acid.** B. B. Baker (Southern Res. Inst., Birmingham, Ala., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1085–1086.—About 0·6% of HF in red fuming HNO_3 can be rapidly determined to within ± 0·05% by measuring the current from the spontaneous electrolysis of the HNO_3 (diluted 500-fold) between an aluminium anode and a platinum cathode. A calibration curve, obtained with 0·3 and 0·8% (w/w) HF standards, is constructed at the beginning of each series of analyses. There is no interference from metallic impurities, and up to 20% of NO_2 can be tolerated.

W. J. BAKER

4104. **Determination of fluoride ion by turbidimetric titration.** W. W. Brandt and A. A. Duswalt, jun. (Dept. of Chem., Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1120–1122.—Milligram amounts of fluoride may be determined rapidly (in < 10 min.) with simple apparatus that is easily assembled from readily available materials. For concn. of F^- of 0·01 to 0·09 *M*, a calcium salt is recommended as titrant, and for the range 0·04 to 1·0 *M* a thorium salt is preferred. The average relative error is then ± 2%. As little as 0·4 mg of F^- may be determined in 2 ml of soln. with a relative error of ± 4%.

K. A. PROCTOR

4105. **Determination of a micro amount of fluoride ion by chelatometric titration.** Kiyoharu Okada and Tsutomu Sugiyama (Yasukawa Plant, Sankyo Co., Shiga-ken). *Ann. Rep. Takamine Lab.*, 1957, **9**, 185–192.—Belcher and Clark's method (*Anal. Chim. Acta*, 1953, **8**, 222) was applied to lower concn. (10 to 200 p.p.m.) of F^-. The best titrating agent is Mg - EDTA, with Eriochrome black T as indicator. The dissociation of CaF_2 near the end-point is avoided by cooling the soln. to between 0° and 5° after the addition of ethanol. The sample soln. containing < 1 mg of F^- is boiled for 15 sec. with $CaCl_2$ soln. (0·0025 *M*, 20 ml), at pH 6·0, mixed with ethanol to produce a 60% ethanolic soln. and kept at 0° to 5° for 2 hr. The cold soln. is titrated with 0·0025 *M* Mg - EDTA soln. (containing ≃ 0·1 g of $MgCl_2$ per litre) in the presence of ethanolamine (1 ml). This method can be satisfactorily applied to the analysis of agricultural chemicals such as fluoroacetamide and $ZnSiF_6$.

K. SAITO

4106. **Spectrochemical determination of fluorine in porcelain enamel frits.** D. C. Spindler and M. F. Smith (Tech. Center, Ferro Corp., Cleveland, Ohio, U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1330–1332.—Fluorine in the range 0·3 to 6% can be determined by this method in which the sample, mixed with $CaCO_3$ and graphite, is excited in a d.c. arc to produce calcium fluoride bands. The intensities of the band head at 5291·00 A, corrected for background,

are compared with those of chemically analysed standards. For 10 samples the average difference between spectrochemical and chemical results was 8%. K. A. PROCTOR

4107. **Determination of total fluoride content in uranium tetrafluoride using ion-exchange columns.** K. F. Sporek (Eldorado Mining and Refining, Ltd., Ottawa, Canada). *Anal. Chem.*, 1958, **30** (6), 1030–1032.—The solid sample of commercial UF_4 is dissolved in a mixture of 25% NaOH and 30% H_2O_2 soln., and after dilution this soln. is passed through a cation-exchange column (Amberlite IR-120, H form, 12 cm), and the HF in the eluate ($\simeq$ 250 ml) is titrated with 0·2 *N* NaOH, with methyl red as indicator. The standard deviation is $\pm$ 0·13 (15 analyses of sample with 23·91% of F), and a result can be obtained in $\simeq$ 20 min. Acids (except H_2CO_3) interfere, but oxides of U do not. The mixture of NaOH and H_2O_2 will dissolve any UO_2, U_3O_8, UO_3 and UO_2F_2 present. The method is also applicable to samples of UF_6 or UO_2F_2.
W. J. BAKER

4108. **Improvements in the analysis of chlorine - hydrogen mixtures, especially technical-grade chlorine from electrochemical plants.** G. Perugini (Montecatini SECL, Bussi, Pescara, Italy). *Chim. e Ind.*, 1958, **40** (1), 16–20.—The apparatus described enables mixtures of H and Cl to be analysed in the absence of light, thus avoiding photosynthesis of HCl, a cause of serious errors. Hydrogen is determined with an accuracy of $\pm$ 0·03%; the apparatus is also suitable for the analysis of technical gases that may contain Cl, HCl and CO_2, O, CO, H and N. C. A. FINCH

4109. **Micro-determination of chloride.** H. Suter and H. Hadorn (Verband Schweizer Konsumvereine, Basle). *Z. anal. Chem.*, 1958, **160** (5), 335–343.—By a modification of Iwantscheff's method of extractive titration with diphenylthiocarbazone (*cf. Angew. Chem.*, 1950, **62**, 361), Cl^- in aq. soln. can be determined with a coeff. of variation of $\pm$4%. *Procedure*—Mix 6 ml of the soln., which should contain 20 to 55 μg of Cl^-, with 0·01 *N* $AgNO_3$ (1 ml) in a Jena filter-tube type 15 G4. After 3 min., apply suction and wash the ppt. with cold H_2O (6 $\times$ 1 ml). Add 4 drops of 50% NaOH soln. and 0·5 ml of 2 *N* formaldehyde and stand the filter in a beaker of boiling water for 3 min. Add 4 ml of H_2O and apply suction. Wash the residue with H_2O (4 $\times$ 1 ml). Dissolve the Ag in 7 drops of HNO_3, add 3 ml of H_2O, apply suction and wash any residue with H_2O (3 $\times$ 1 ml). Transfer the soln. to a separating funnel and titrate extractively with diphenylthiocarbazone, with CCl_4 as the solvent. All ions that yield sparingly soluble compounds with Ag interfere. G. BURGER

4110. **Determination of traces of iodine.** K. Komárek (Res. Chem. Lab. of Nat. Museum, Prague). *Chemie, Prague*, 1958, **10** (2), 105–112.—A survey of micro-methods suitable for the determination of iodine in inorganic and organic materials. (22 references.) J. ZÝKA

4111. **Determination of iodate and periodate ions in the presence of each other.** L. Szekeres, E. Kardos and M. Rády (Univ. für Landwirtschaftwissenschaften, Budapest). *Z. anal. Chem.*, 1958, **160** (6), 401–403.—To one portion of the sample are added KI and HCl and the total of IO_4^- and IO_3^- is determined by titration with $Na_2S_2O_3$. In another portion the IO_4^- are reduced to IO_3^- by the addition of KBr and HCl. The soln. is made alkaline with $NaHCO_3$ and the resulting NaOBr is reduced to NaBr by boiling with ethanol. The IO_3^- remaining are determined iodimetrically.
G. BURGER

4112. **New method for the determination of iodate and bromate in their mixtures.** P. A. Epik and A. I. Orochko. *Izv. Kievsk. Politekh. Inst.*, 1957, **20**, 90–94; *Ref. Zhur., Khim.*, 1958, Abstr. No. 28,489.—A rapid and accurate method for the determination of BrO_3^- and IO_3^- when present together in any quantities is based on their different stabilities in acid. Boil 20 ml of soln. for 10 min. with 20 ml of conc. H_2SO_4 (completely decomposing the BrO_3^- and leaving the IO_3^- unchanged), cool, dilute to 100 ml, add KI and titrate the liberated iodine with $Na_2S_2O_3$ soln. Determine BrO_3^- by the difference of the results obtained by titration of total BrO_3^- and IO_3^- without boiling the soln. with H_2SO_4, and titration of IO_3^- alone after boiling with H_2SO_4. C. D. KOPKIN

4113. **Photometric determination of manganese in ignited magnesia and chalk.** L. L. Bogina and I. P. Martyukhina. *Kauchuk i Rezina*, 1957, (8), 32–33; *Ref. Zhur., Khim.*, 1958, Abstr. No. 21,179.—A photometric variation of the persulphate - cobalt method (*Ref. Zhur., Khim.*, 1953, 663) has been developed, and used in the analysis of MgO and chalk. Dissolve 5 g of MgO in 60 ml of 12% (v/v) H_2SO_4, or boil 2 g of chalk in a covered beaker with 60 ml of 6% (v/v) H_2SO_4 for 15 to 20 min. Filter the resulting soln. and wash the filter with boiling water three or four times (5 to 7 ml). To the filtrate add H_3PO_4 (sp. gr. 1·70, 1 ml), a soln. of a cobalt - nickel catalyst (0·5 g of $CoSO_4.7H_2O$ and 1·5 g of $NiSO_4$ in 100 ml of water) (10 ml) and a freshly prepared soln. of $(NH_4)_2S_2O_8$ (10 ml). Boil for 2 or 3 min. to obtain a stable MnO_4^- colour and keep on a boiling-water bath for several minutes till the $(NH_4)_2S_2O_8$ is decomposed. Cool the soln., make up to 100 ml and measure the extinction with a green filter, with water as comparison soln. For calibration curves use $KMnO_4$ soln. (0·1 mg of Mn per ml), previously decolorised with H_2O_2. The results obtained agree well with those of the persulphate - silver method.
C. D. KOPKIN

4114. **Rapid determination of manganese in ferromanganese and tungsten tool steels.** C. O. Ingamells and W. S. Bradshaw (Rock Analysis Lab., Univ. of Minnesota, Minneapolis, U.S.A.). *Chemist Analyst*, 1958, **47** (1), 11–12.—Transfer 0·3 g of ferromanganese (< 100 mesh) to a 500-ml flask, wash down with 5 ml of H_2O, 1 ml of conc. HNO_3 and 6 ml of 72% $HClO_4$ and heat gently without swirling till dissolution is complete except for carbon, but do not allow the soln. to fume. Add 50 ml of 85% H_3PO_4, heat on a hot-plate till foaming has ceased and the soln. assumes a deep-purple colour, wash down with 15 ml of H_3PO_4 without swirling, and discontinue heating when boiling ceases and most of the $HClO_4$ has fumed off. The heating period is judged by experience. It must not be so prolonged as to cause insoluble material to separate, but in the presence of Cr must be continued till CrO_4^- are converted into Cr^{3+}. Allow the soln. to cool slowly till the flask can be

handled but is not quite cold, then add 15 ml of cold water, mix, cool thoroughly, add 150 ml of water and cool at once in running water. Titrate with 0·1 *N* $(NH_4)_2SO_4.FeSO_4$ till the pink colour due to Mn is nearly discharged, add a few drops of 1% diphenylamine in conc. H_2SO_4 and continue titration until the indicator colour disappears. The end-point is very sharp and gives little warning. Calculate the Mn on the basis of a standard ferromanganese treated similarly, and correct for V, which is determined separately. Results agree well with those by the bismuthate procedure. With tungsten tool steels, the acid mixture for dissolution must be varied according to composition of the metal. Thus, 2 g of a steel containing Cr and W is treated with 15 ml of $HClO_4$ and 50 ml of H_3PO_4.

R. E. ESSERY

4115. **Separation of rhenium by co-precipitation and its determination in molybdenite.** Jen-Yin Yen and Tseng-Ning Tao (Dept. of Chem., Peking Univ.). *Acta Chim. Sinica*, 1958, **24** (1), 97–104.—Rhenium (10 to 100 μg as perrhenate) can be completely co-pptd. in neutral, acid or alkaline soln. with tetraphenylarsonium perchlorate, prepared from 1% $KClO_4$ and 0·7% tetraphenylarsonium chloride soln. (**I**) (*cf.* Willard and Smith, *Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 305). The recovery of added Re is > 99%. When the test is carried out in 50 ml of soln. containing NaCl (1 g) and NaOH (1 g), and the ppt. is washed with 0·5% NaOH soln. containing **I**, perrhenate can be separated from large amounts of molybdate (⩾ 0·88 g of Mo). The washed ppt. is freed from molybdate by dissolving it in hot water, adding more **I** and $KClO_4$ soln. and cooling the mixture to room temp. Zincate, aluminate, nitrate, phosphate, arsenite, arsenate, vanadate, selenite, chromite, chromate and tungstate do not interfere. Rhenium is brought into soln. by treating the ppt. with hot water and excess of $KClO_4$, and may be determined colorimetrically by a method based on the Geilmann reaction (*cf.* Hurd and Babler, *Brit. Abstr. A*, 1936, 580). The method has been applied successfully to the determination of Re in molybdenite. The results compare well with those of the distillation method. A complete analysis takes just over 2 hr.

S. H. YUEN

4116. **Extraction of ferric chloride with *iso*butyl methyl ketone and amyl acetate.** A. Claassen and L. Bastings (N. V. Philips' Gloeilampenfabrieken, Eindhoven-Netherlands). *Z. anal. Chem.*, 1958, **160** (6), 403–409 (in English).—Ferric chloride is extracted from soln. in 7 *N* HCl by a mixture of *iso*butyl methyl ketone and amyl acetate in the proportion 1 + 1 or 1 + 2. This mixture has the advantages that it gives a high distribution ratio (approx. 4000), it does not form emulsions and the phases are easily distinguished. One extraction removes Fe quantitatively. The extraction should be carried out in a cylinder and the soln. transferred to a tap-funnel after the phases have separated. The $FeCl_3$ can be extracted from the solvent by shaking with water. This method is applicable to the determination of Fe in all concn. up to 2%, and to the removal of Fe to prevent interference in the determination of other metals. The behaviour of 44 elements with this solvent system has been investigated. G. BURGER

4117. **Application of electrographic analysis to the identification of the principal elements of steel alloys.** B. Medianu, V. Manu, O. Butaliu and V. Korony. *Rev. Chim., Bucharest*, 1958, **9** (2), 103–104.—The method is based on the anodic dissolution of the sample and the capture of ions formed on filter-paper soaked with electrolyte or electrolyte plus a reagent. The electrogram is developed and fixed with the appropriate reagent. Nickel is identified with dimethylglyoxime; Mo by the formation of a thiocyanate carmine rose complex $[MoO(SCN)_4]^{2-}$; Cr by oxidation of Cr^{3+} to CrO_4^{2-}, which is used to oxidise benzidine. The method is suitable for only approx. estimations of Ni, Mo and Cr. H. SHER

4118. **Routine determination of oxygen in steel using a carrier-gas fusion technique.** C. E. A. Shanahan and F. Cooke (Richard Thomas and Baldwins, Ltd., Aylesbury, England). *J. Iron St. Inst.*, 1958, **188** (2), 138–142.—The vacuum-fusion method for the determination of O in steel has not been generally adopted by steelworks owing to the fragility of the apparatus and the difficulties of high-vacuum technique, etc. A method has therefore been developed in which the CO evolved when the sample (≃ 120 g) is melted in a crucible is extracted by a stream of carrier gas (argon) and is then oxidised by passage over a mixture of CuO and Fe_2O_3 held at 550°. The determination may be made in 15 min. with a precision equal to that of the vacuum-fusion method and a standard deviation of ≃ 0·0016% of O. The equipment, which is described, is inexpensive, and easily operated and repaired under works conditions. The blank rate is high but is reasonably constant and therefore does not give rise to any appreciable error.

J. M. JACOBS

4119. **Evaluation of inert-gas fusion method for rapid determination of oxygen in steel.** J. I. Peterson, F. A. Melnick and J. E. Steers, jun. (Graham Res. Lab., Jones & Laughlin Steel Corp., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1086–1089.—The content of O in most samples of steel can be determined in ≃ 7 min. by a simplification of the capillary-trap apparatus and procedure of Smiley (*cf. Anal. Abstr.*, 1956, **3**, 93). The modifications are (*i*) the elimination of the argon-purification and pressure-regulation systems, commercial argon being pure enough, (*ii*) use of an all-metal system, (*iii*) substitution of high-purity graphite (20 mesh) for the Sn used as flux, and (*iv*) elimination of the water absorbent beyond the furnace. The oxidation reagent (I_2O_5) is retained, and the crucible is operated at ≃ 1700°. The results agree with those obtained by vacuum fusion and are satisfactory provided that an excess of graphite particles is always kept in the crucible.

W. J. BAKER

4120. **Effect of nitrides in silicon iron on the determination of oxygen by chlorination, and the possible direct determination of aluminium nitride.** F. J. Armson and H. L. Bennett (G.K.N. Group Res. Lab., Wolverhampton, England). *J. Iron St. Inst.*, 1958, **188** (2), 132–137.—When steel is heated in chlorine, the metallic elements present form volatile chlorides, while the oxides are virtually unattacked. This principle was developed into an analytical method for the determination of total O in fully-killed mild steels and certain low-alloy steels, but co-operative analyses showed serious inconsistencies in the amount of the individual oxides. This difficulty was overcome by a special chlorination technique developed by Short *et al.* [*J. Iron St. Inst.*, 1957, **186** (1), 85]. In

extending the method to silicon irons an important source of error was discovered, namely the survival of substantial amounts of AlN after chlorination. Owing to the stability of the AlN the amount of Al subsequently determined in the residue will be considerably higher than that due to Al_2O_3 alone and hence the O content finally calculated from this figure will be too high. In order to correct for this error the N in the residue must be determined and the amount of Al required to combine with it must be found. The difference between this and the total Al in the residue gives the true amount of Al in combination as Al_2O_3. Most of the AlN present in silicon iron is retained in the residue obtained after chlorination for 20 hr. at 500°, but TiN and TiC, present in solid solution, are completely decomposed and this, together with other evidence, suggests that the determination of AlN is possible by the chlorination technique.

J. M. JACOBS

4121. **Determination of carbon in steel by combustion and conductimetry.** R. Boulin (Inst. de Rech. de la Sidérurgie, St. Germain-en-Laye, France). *Chim. Anal.*, 1958, **40** (3), 72–76.—Apparatus is described and illustrated in which the steel is burnt in a stream of O, and the CO_2 is absorbed in 0·005 *N* NaOH in one half of an equilibrated conductivity cell, the absorption giving rise to a disequilibrium which is measured by an electronic recorder, response being linear up to 250 μg of C. The sample is burnt at 1400° in a porous thimble placed in a boat in the specially shaped combustion tube; the O is purified with Ascarite - anhydrone, and S is removed with granular silver orthovanadate. A system of pumps withdraws the gas from the combustion tube and passes a predetermined fraction through the absorption cell so that the upper limit of 250 μg of C is not exceeded. Calibration is carried out with samples of known content of C. The interpretation of the curves is discussed. Replicate analyses of low-carbon steels gave errors in the range ± 4·1 to 5·7% of the content of C. Collaborative analyses of a steel containing 30×10^{-3}% of C gave a standard deviation of $1{\cdot}7 \times 10^{-3}$ for conventional methods and $0{\cdot}65 \times 10^{-3}$ for the present one. As little as 4 μg per litre of CO_2 in the exit gases can be measured. A low-carbon ordinary steel can be analysed in 4 min., and an alloy steel in 6 min., from introduction of sample to reading of result.

R. E. ESSERY

4122. **Quantitative spectral determination of small amounts of boron in steel.** J. Jindra (Res. Inst. of Iron Metallurgy, Prague). *Hutn. Listy*, 1958, **13** (1), 53–56.—By means of differences in solubility of boron in HCl, it is possible to determine the content of sol. and insol. boron in minute amounts in steel, with the use of solution-spectrographic analysis. For the separation of boron from Fe and other elements, the distillation method with methanol was used. The spectrographic determination was carried out by means of a rotating carbon electrode. Zinc was used as internal standard. The lines measured were B 2497·73 - Zn 2502·00 A. The methods enable boron to be determined with an accuracy of ±0·0003% of B. J. ZÝKA

4123. **Photometric determination of aluminium in alloy steels.** H. Lilie and H. Rosin (Dtsch. Amt für Material- und Warenprüfung, Halle, Saale). *Z. anal. Chem.*, 1958, **160** (4), 261–267.—Interference by Cr in the method previously described (Lilie, *Anal. Abstr.*, 1958, **5**, 1222) can be reduced by correct choice of (*a*) the concn. of Eriochrome cyanine in the reaction mixture and (*b*) the concn. of Cr in the blank soln. A. R. ROGERS

4124. **The rapid determination of magnesium in iron.** R. Reichert. *Giesserei*, 1957, **44** (2), 51–52.—Magnesium is determined with EDTA after the separation of Fe with $(NH_4)_2S$. *Procedure*—Dissolve the sample (1 g for Mg > 0·01%, 5 g for Mg < 0·005%, 10 g for Mg (< 0·001%) in HCl (plus HNO_3, if necessary), make the hot soln. ammoniacal and add 1 to 2 g of NH_4Cl. Pass H_2S. Filter under suction and wash the ppt. once. To the hot filtrate add 1 g of ascorbic acid, 10 ml of 10% KCN soln. and 2 ml of 50% v/v triethanolamine. Add a further 0·5 g of ascorbic acid, solid Eriochrome black T indicator (1% in NaCl) and adjust to pH 10 with aq. NH_3. Titrate at 60° with 0·01 *M* EDTA. The mean error on 0·1 to 5 mg of Mg is 0·7%.

T. R. ANDREW

4125. **Variation of the method for the rapid determination of aluminium in high-alloy steels.** V. F. Mal'tsev. *Byull. Nauch.-Tekh. Inform. Vses. Nauchi Trubnyĭ Inst.*, 1957, (3), 108–110; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,549.—A variation of the earlier photometric determination of Al [Temirenko, *Zavod. Lab.*, 1947, (5), 621] after its separation on the mercury cathode is described. Dissolve 0·1 g of steel in 10 ml of H_2SO_4 (1:6), make up to 100 ml, filter, discarding the first portions of filtrate, neutralise a 25-ml aliquot with 15% aq. NH_3, add 0·5 ml of H_2SO_4 (1:6), and electrolyse with a mercury cathode for 30 min. at 0·08 amp. per sq. cm. After the electrolysis, without breaking the current, transfer the soln. to a 250-ml flask and wash the cathode three times with water (20 to 25 ml). Filter the soln., add 2 drops of a 0·1% aq. soln. of Tropaeolin OO, neutralise with 15% aq. NH_3 and make up to 200 ml. To 20 ml of the soln. add 12·5 ml of acetate buffer soln. (0·2 *M* Na acetate - 0·2 *M* acetic acid, equal vol.) and 1 ml of a 0·1% aq. aluminon soln., mix, warm for 5 min. at 90°, cool rapidly, make up to 50 ml with the buffer soln., mix and measure the extinction with a green filter. A method of purifying mercury is described.

C. D. KOPKIN

4126. **Rapid photometric determination of aluminium in steel and cast iron.** V. D. Konkin. *Byull. Nauch.-Tekh. Inform. Ukr. Nauch. Inst. Metallov*, 1957, (2), 76–81; *Ref. Zhur., Khim.*, 1958, Abstr. No. 24,763.—In determining Al in the presence of Fe with aluminon (**I**), Fe^{3+} are reduced with hydroxylamine sulphate (**II**). The presence of excess of **II** (up to 10 ml of a 20% soln. of **II**) has little influence on the light absorption of soln. of **I**. The extinction of the soln. being analysed increases mainly in the first 15 min. and becomes stable after 90 min. The most intense colour of the complex of Al and **I** is found at pH 5·0 to 5·2. The influence of a series of ions on the determination of Al with **I** is studied. The presence of up to 0·7% of Be, 8% of V and large amounts of Cr does not cause interference; interference is caused by > 15 μg of Ti in 50 ml of soln. Beer's law is obeyed up to 49 μg of Al. On the basis of the results obtained, a rapid (40 or 45 min.) method is evolved for the determination of Al in steel and cast iron.

C. D. KOPKIN

4127. **Colorimetric determination of large contents of silicon in high-alloy steels and fluxes for electro-welding.** V. F. Mal'tsev and L. P. Luk'yanenko. *Trudy Nauch.-Tekh. Ob. Chernoĭ Metallurg., Ukr. Resp. Pravl.*, 1956, **4**, 111–114; *Ref. Zhur., Khim.*, 1958, Abstr. No. 24,820.—A method is described for the photometric determination of Si as the complex silicomolybdenum blue after solution of SiO_2 by successively treating the soln. to be analysed with alkali and acid. To determine Si in high-alloy steels, dissolve 0·1 g of steel in a mixture of conc. HNO_3 and conc. HCl (1:1, 10 ml), transfer the soln. to a platinum dish containing 35 ml of 10% NaOH soln., heat for 3 min., cool, add conc. HNO_3 (15 ml), cool and make up to 200 ml. To 1 ml of the resulting soln. add 0·125 *N* H_2SO_4 (20 ml) and 5% $(NH_4)_2MoO_4$ soln. (2·5 ml), set aside for 3 min., add 8 *N* H_2SO_4 (7·5 ml), set aside for 1 min., introduce a 4% soln. of $(NH_4)_2SO_4.FeSO_4$ (10 ml), stir, make up to 50 ml, mix, and measure the extinction 3 min. after adding the $(NH_4)_2SO_4.FeSO_4$, with a red filter. A blank is carried out concurrently. To determine Si in fluxes, fuse 0·1 g of finely ground flux with 4 g of K_2CO_3 and 2·5 g of borax for 15 or 20 min. at 900° to 950°. Dissolve the melt in 350 ml of water, 10 ml of HNO_3 (sp. gr. 1·4) and 50 ml of saturated oxalic acid soln. (to reduce Mn), heat to dissolve, then cool the soln. and make up to 500 ml. To 3 ml add 0·15 *N* H_2SO_4 (17 ml) and a 5% soln. of $(NH_4)_2MoO_4$ (5 ml), set aside for 3 min., add 8 *N* H_2SO_4 (15 ml), $CuSO_4$ soln. (5 mg of Cu per ml, 5 ml) and a 7% soln. of thiourea (20 ml), mix and measure the extinction with a red filter. Carry out a blank concurrently. C. D. KOPKIN

4128. **Determination of titanium in steel by amperometric titration with cupferron.** Yu. I. Usatenko and G. E. Bekleshova. *Trudy Nauch.-Tekh. Ob. Chernoĭ Metallurg., Ukr. Resp. Pravl.*, 1956, **4**, 39–43; *Ref. Zhur., Khim.*, 1958, Abstr. No. 28,433.—The method is based on the direct amperometric titration of Ti with a soln. of cupferron (**I**) to the appearance of a diffusion current on a rotating platinum electrode. Dissolve 0·2 to 2 g of steel, containing 0·5 to 0·01% of Ti, by warming with H_2SO_4 (1:1) and add 0·1 *M* $FeCl_3$ (0·5 ml) and a 0·3% soln. of **I** (5 ml). Filter, and wash the ppt. Dissolve in ≃ 10 ml of hot 6 *N* H_2SO_4, boil, add a little $(NH_4)_2S_2O_8$, evaporate to fumes of SO_3, dilute with water, nearly neutralise with aq. NH_3, add Na_2SO_3, boil to remove SO_2 and cool. Insert in the soln. a rotating platinum microelectrode and the bridge of a S.C.E., and establish a potential of + 0·85 V. The pointer of the galvanometer goes off the scale because of the presence of Fe^{3+} in the soln. To oxidise the iron add a dilute ammonium vanadate soln. dropwise till the pointer returns to the end of the scale. Neutralise the soln. with aq. NH_3 in the presence of 1 drop of a 0·1% soln. of methyl violet to a stable green colour (pH 1·0 to 1·5), add a 1% soln. of EDTA (disodium salt) (10 ml) and NH_4Cl (3 to 4 g) and titrate with a soln. of **I** to a sharp increase in the diffusion current. Draw the titration curve and calculate the percentage of Ti. The described method can be used for any concn. of Ti in steel down to 0·001%. It is established that in separating Ti from the major portion of Fe by the addition of a minimal amount of **I**, there is first pptd. the cupferron complex of Ti, and then that of Fe^{3+}; with a very large excess of Fe^{3+} there is no formation of cupferron complexes as ppt. C. D. KOPKIN

4129. **Volumetric determination of phosphorus and arsenic in plain steel by the differential method with quinoline and ammonium molybdates.** S. Meyer and O. G. Koch (Neunkircher Eisenwerk A.-G., Neunkirchen, Saar). *Z. anal. Chem.*, 1958, **160** (4), 253–258.—The concn. of P and of As in steel can be determined by this method to within ± 0·0002% and ± 0·0005%, respectively. The time taken for the simultaneous determination is 20 min. *Procedure*—Dissolve the sample (1 g) by heating with H_2O (50 ml), $KClO_3$ (6 g) and conc. HCl (10 ml). Boil, add 10% tartaric acid soln. (20 ml) and quinoline molybdate reagent (20 ml) (*cf.* Fernlund and Zechner, *Anal. Abstr.*, 1955, **2**, 2695). Transfer the ppt. to a filter with dil. HCl and wash free from acid with H_2O. Suspend the ppt. in CO_2-free H_2O (50 ml), dissolve it in a known excess of 0·1 *N* NaOH and titrate with 0·1 *N* HCl, with phenolphthalein as indicator. Perform a blank titration. This gives the total of P and As. Determine P alone with ammonium molybdate in a similar manner. A. R. ROGERS

4130. **Investigation of a method for the combined determination of niobium and tantalum in steel.** B.I.S.R.A. Methods of Analysis Committee. *J. Iron St. Inst.*, 1957, **187** (4), 341–343.—The Bagshawe and Elwell method (*J. Soc. Chem. Ind.*, 1947, **66**, 398) was investigated and approved. In this procedure, a soln. of the sample in aq. HCl is treated with an excess of H_2SO_3, the ppt. is fused with K_2CO_3, and the melt, after extraction with water, is treated with $MgSO_4$ - NH_4Cl to precipitate quant. Nb, Ta and Ti. The Ti is determined colorimetrically and the combined Nb and Ta calculated by difference. C. H. COWPER-COLES

4131. **Determination by automatic coulometry of chromium, manganese and vanadium in steel.** A. Liberti and L. Ciavetta. *Metallurg. Ital.*, 1958, **50** (2), 50–52.—These metals can be determined automatically by coulometry by electrolytic reduction from their maximum oxidation state. A 100% current efficiency in the reduction process is obtained by using as electrolyte a soln. containing Fe^{3+}. An amperometric end-point has been used with a rotating platinum electrode polarised at + 1·0 V *vs.* the S.C.E. The diffusion current, due to Fe^{2+}, stops the generating current automatically by means of an electronic relay. N. E.

4132. **Photometric determination of cobalt.** F. da Silva. *Técnica, Lisbon*, 1957, **31** (271), 471–474; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,567.—The method is based on the formation by Co of a coloured complex with EDTA (disodium salt) (**I**) and H_2O_2 in ammoniacal medium. To ≃ 25 ml of soln. (1 to 15 mg of Co^{2+}) add *M* **I** (10 ml), aq. NH_3 (1:1) (4 ml) and 3% H_2O_2 soln. (5 ml), make up to 50 ml and after 5 min. measure the extinction at 580 mμ. The colour is stable for 1 hr. Ions of Fe, Ti, Ni and Cu interfere, but SO_4^{2-} and F^- interfere only at concn. > 100 mg in 50 ml.

C. D. KOPKIN

4133. **Redox behaviour of cobalt chelates of nitrilotriacetic acid.** K. L. Cheng (Westinghouse Electric Corp., East Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1035–1039.—In the presence of 0·5 *M* nitrilotriacetic acid (**I**), oxidation of Co^{2+} or Fe^{2+} with H_2O_2 in alkaline soln. produces a deep-violet colour, but with sodium perborate only Co gives the colour. No other metals give this reaction; the cobaltic - **I** complex has max.

extinction at 560 mμ and follows Beer's law for concn. of 0·01 to 0·4 millimole of Co per 50 ml in H_3PO_4 soln. and for concn. of 0·01 to 0·1 millimole of Co per 50 ml in Na_2CO_3 soln. Factors affecting colour formation, pH, time, temp., and analytical application to the determination of Co, H_2O_2, **I**, Na_2O_2 and sodium perborate are discussed.

W. J. BAKER

4134. Colorimetric micro-determination of cobalt and copper with sodium 4-aminosalicylate. R. Ralea and N. Iorga (Univ. "Al. I. Cuza," Iaşi, Romania). *An. Ştiinţ. Univ. "Al. I. Cuza" din Iaşi, Sect. I*, 1956, **2** (1–2), 211–226.—*Procedure for cobalt*—The method is based on the measurement of the brown colour obtained by the oxidation of Co^{2+} with Na_2O_2 in the presence of Na 4-aminosalicylate (**I**). To a few ml of a soln. containing 0·003 to 0·3 mg of Co are added 5 ml of 0·4 *M* **I**, 10 ml of 4 *M* NaOH, and a few granules of Na_2O_2. After 10 min., when the colour reaches its max. intensity, 0·75 ml of *M* Na_2SO_4 is added, the liquid is diluted to 25 ml with water, and the colour is measured in a colorimeter, with a green filter. This colour is then compared with the standard tables given. It remains stable for 30 min. The method can be used for concn. of 0·1 μg to 12 μg of Co per ml, and in the presence of Fe (1:40); Mn (1:60); Pb, Sn and V (1:1000); Cr (1:600); and Ni (1:70). Copper interferes seriously. *Procedure for copper*—To a few ml of a soln. containing 0·008 to 0·8 mg of Cu are added 5 ml of 0·4 *M* **I**, 10 ml of 4 *M* NaOH and 0·15 to 0·2 g of Na_2O_2, and, after 20 min., 1·25 ml of *M* Na_2SO_3. The whole is diluted to 25 ml and the deep-brown colour is measured, with a green filter, within 30 min. and compared with standard tables. The method can be used down to a concn. of 0·033 mg per ml and in the presence of Fe (1:40); Pb and Sn (1:100); and Cd (1:60). Arsenic and Co interfere.

H. SHER

4135. Spectrographic analysis of nickel in quartz, pyrites and chalcopyrites. K. P. Puzanova. *Trudy Sverdl. Gorn. Inst.*, 1957, (30), 68–75; *Ref. Zhur., Khim.*, 1958, Abstr. No. 35,917.—In order to investigate the influence of the composition and form of the molecular compounds on the intensity of the Ni line, test samples have been prepared with quartz, pyrites and chalcopyrites containing 0·001 to 0·3% of Ni in the form of $NiCO_3$, NiO and $NiCl_2$. The spectra were excited by an a.c. arc by the evaporation of the sample on carbon electrodes. In order to increase the sensitivity of the determination of Ni in the samples it is necessary to introduce quartz or carbon powder in a 2:1 ratio. The intensity of Ni lines **3619·3**, **3414·7**, **3452·8**, **3052·8** and **3003·6** A depends very little on the type of molecule containing Ni. The current strength should be 7 to 8 amp. in order to compensate for the differences in the volatility of the substances.

W. ROUBO

4136. Volumetric determination of nickel in catalyst powders. O. N. Dobrynina and K. G. Bogareva. *Maslob.-Zhir. Prom.*, 1957, (9), 40; *Ref. Zhur., Khim.*, 1958, Abstr. No. 21,183.—The method is based on the complexometric titration of Ni^{2+} in the presence of murexide (**I**) as indicator. Dissolve 2 g of the powder by boiling with HCl (1:1), continuing the heating till no more gas is evolved. Cool, make up to 250 ml (if the soln. is cloudy, filter it), take a 10-ml aliquot, add water (30 ml), aq. NH_3 (1:5) (20 ml), and a little **I** (0·2 g of **I** mixed with 10 g of NaCl) and titrate with 0·1 *N* EDTA (disodium salt) till the colour changes from green to violet. The EDTA soln. is standardised against a soln. of a catalyst salt of known content of Ni. The results obtained in the determination of Ni in copper - nickel powders agree satisfactorily with those of the gravimetric dimethylglyoxime method. The described method has the advantages that the time for the analysis is shortened (to 1 or 1·5 hr.), it is cheaper, and does not require the use of ashless papers or porcelain crucibles. The method may also be used for determining Ni in used catalysts.

C. D. KOPKIN

4137. Determination of nickel in zirconium and "zircaloy." M. Rastoix. *Rapp. Cent. Ét. Nucl., Saclay*, 1957, (698), 6 pp.—The rapid method given will determine from 10 to 200 μg of Ni in 50 ml of soln. *Procedure*—Dissolve the sample (0·25 to 0·5 g) in H_2O (10 ml) and conc. HF (1 ml), with HNO_3 (2 or 3 drops) if Sn is present. Add 20% aq. citric acid (5 ml) and then conc. aq. NH_3 (≃ 6 ml) until the soln. is alkaline. Cool and add 0·1% ammoniacal dimethylglyoxime soln. (8 ml) followed immediately by bromine water (5 ml). Make the vol. up to 50 ml and, within ⩾ 20 min., measure the extinction of the wine-red complex at 440 mμ in a 1-cm cell. Approx. max. permissible amounts of interfering metals are Zr (0·5 g), Sn (10 mg), Fe (1000 μg), Cu (315 μg) and Cr (210 μg).

W. J. BAKER

4138. Spectrochemical analysis of nickel alloys for the cathodes of electronic tubes. L. Vecsernyés (Forschungsinst. für Fernmeldetech., Budapest). *Z. anal. Chem.*, 1958, **160** (5), 332–335.—Amounts of 0·001 to 1% of Zn, Pb, Mg, Al, Cu, Mn, Fe, Cr and Co in nickel alloys can be determined within ± 5% by spectral analysis in soln. The sample (2 mg) is dissolved in HCl, and HNO_3 is added drop by drop. Any W present is thus pptd. as H_2WO_4, filtered off, ignited and weighed as WO_3. The filtrate is evaporated and dissolved in *N* HCl to make a soln. containing 40 g of Ni per litre. The spectrogram is made with an interrupted a.c. arc by the drop method. Comparison soln. are made by adding metal salts to a nickel soln. from which all impurities have been successively pptd. This method is not suitable for the determination of Ti and Si because of the difficulty of obtaining sufficiently pure electrode carbons.

G. BURGER

4139. Determination of nickel in the presence of large amounts of copper. I. Atanasiu, M. Popescu and A. Căluşaru. *Rev. Chim., Bucharest*, 1957, **8** (12), 775–777.—The Cu is first removed by electrodeposition from a H_2SO_4 soln. at < 2·3 V. The excess of acid in the remaining soln. of nickel sulphate is neutralised by the addition of excess of conc. aq. NH_3. Oxygen is then removed by the addition of a few crystals of Na_2SO_3, and the nickel soln. is determined polarographically, with an error < ± 1%. Standard soln. of Ni can be prepared from the Ni that has been electro-deposited on copper cathodes (when the determination of Ni is being made in the presence of large amounts of Cu) or on platinum cathodes.

H. SHER

4140. Colorimetric determination of nickel in products from copper production. L. N. Krasil'nikova. *Sb. Trud. Vses. Nauch. Inst. Tsvet. Met.*, 1956, (1), 165–168; *Ref. Zhur., Khim.*, 1958, Abstr. No. 21,182.—In the determination of Ni with dimethylglyoxime (**I**), the Ni is separated from Cu

and other elements by extraction with CCl_4 instead of $CHCl_3$. Treat 1 g of slag from the furnace or converter (or 1 g of dust from the furnace or 0·2 g of matte) by heating it successively with HCl (sp. gr. 1·19) (10 ml), HNO_3 (sp. gr. 1·4) (5 ml) and H_2SO_4 (1:1) (5 or 10 ml). Evaporate the soln. to SO_3 fumes, add 50 ml of water, cool, filter off $PbSO_4$, and wash the insoluble residue 4 or 5 times with cold water acidified with H_2SO_4. Combine the filtrate and wash liquors and make up to 100 ml. To an aliquot (20 ml for furnace slags, 10 ml for converter slags and furnace dusts, and 5 ml for matte) in a 50-ml separatory funnel add 50% citric acid soln. (5 ml), neutralise to litmus with aq. NH_3, cool, add a 1% ethanolic soln. of **I** (4 ml) and CCl_4 (3 ml) and shake for 1 min. Extract the ammoniacal layer with a further 2 ml of CCl_4, combine the organic soln., add 0·5 *N* HCl (5 ml) and shake for 1 min. Repeat the washing with a further 5 ml of 0·5 *N* HCl, combine the acid soln., heat to remove drops of CCl_4, cool, neutralise to litmus with 20% NaOH soln. and add 1 ml in excess. Add 2·5 ml of a 3% soln. of $(NH_4)_2S_2O_3$, mix, add 2·5 ml of a 1% ethanolic soln. of **I**, mix, and dilute to 25 ml, and after 5 to 7 min. measure the extinction with a blue filter, with a blank treated as above for comparison soln. To construct a calibration curve use a soln. of concn. 0·01 mg of Ni^{2+} per ml. The method gives reproducible and satisfactorily accurate results, and may be used for the determination of Ni in blister copper.

C. D. KOPKIN

4141. **Determination of nickel, boron and fluorine in nickel hydroxyfluoroborate electrolytes.** K. A. Nesmeyanova. *Trudy Gos. Nauch. Inst. Khim. Prom.*, 1956, **4**, 55–60; *Ref. Zhur., Khim.*, 1958, Abstr. No. 21,204.—A method is described for the determination of total Ni and B, for the determination of F present as BF_4^-, and, with certain approximations, as BF_3OH^-. Determine Ni by titration with an alkaline soln. of dimethylglyoxime, and B by titration with NaOH soln. to phenolphthalein after destroying the hydroxyfluoroborate complex anions and formation of free boric acid. The determination of F present as BF_3OH^- is based on titration of the HCl liberated in amount equiv. to the BF_3OH^-, in the cold, by the reaction—

$$Ni(BF_3OH)_2 + 3CaCl_2 + 4H_2O = 2H_3BO_3 + 3CaF_2 + NiCl_2 + 4HCl$$

(the decomposition of BF_4^- in the cold takes place slowly). The determination of F present as BF_4^- is based on the titration of the HCl, liberated in amount equiv. to the BF_4^-, by boiling, according to the reaction—

$$Ni(BF_4)_2 + 4CaCl_2 + 6H_2O = 2H_3BO_3 + 4CaF_2 + NiCl_2 + 6HCl.$$

In practice, the determination of F present as BF_3OH^- is carried out by titration of an aliquot of the electrolyte with NaOH soln. to methyl red in the cold after addition of $CaCl_2$, and that present as BF_4^- by titration of the same soln. with alkali after boiling.

C. D. KOPKIN

4142. **Circular-paper chromatography in the separation of ions. Separation of precious metals.** A. K. Majumdar and M. M. Chakrabartty (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1958, **18** (3), 193–196.—The R_F values for Pd^{2+}, Pt^{4+}, Ir^{4+}, Rh^{3+}, Ru^{3+}, Os^{4+} and Au^{3+} are determined, the chromatograms being developed with 16 solvent mixtures. Suitable conditions are found for the separation of some ternary and quaternary mixtures of the metals.

W. C. JOHNSON

4143. **Identification of ruthenium species in aqueous solution.** H. H. Cady and R. E. Connick (Dept. of Chem. and Radiation Lab., Univ. of Calif., Berkeley, U.S.A.). *J. Amer. Chem. Soc.*, 1957, **79**, 4242–4243.—The ionic charge per atom of Ru (*a*) is measured by means of an ion-exchange method. The ruthenium ions are eluted from a column by means of cerous perchlorate. The net ionic charge of Ru (*b*) is found by finding the concn. dependence of the exchange of Ru with H^+. The ratio of *b* to *a* gives the number of atoms of Ru per species, *i.e.*, the degree of polymerisation.

C. A. SLATER

4144. **Salts of N-substituted dithiocarbamic acids and their use in the determination of rhodium and iridium.** N. K. Pshenitsyn and N. V. Fedorenko. *Zhur. Neorg. Khim.*, 1957, **2** (10), 2375–2382; *Ref. Zhur., Khim.*, 1958, Abstr. No. 28,458.—The determination of Rh and Ir by pptn. with ammonium *p*-aminophenyldithiocarbamate (**I**) has been studied. From HCl soln. Rh and Ir are quant. pptd. on warming, but the ppt. formed must be coagulated by the addition of methyl violet. Rhodium is quant. pptd. at pH 2 to 7, and Ir at pH 3 to 5. The composition of these compounds is M:**I** = 1:3. The separation of Rh and Ir cannot be achieved with **I**, since both metals react with **I** under approximately the same conditions.

C. D. KOPKIN

4145. **5-Aminothiazoline-2-thiocarboxyamide used as analytical reagent. I. Detection and determination of palladium.** Ping-Shih T'ien and K'uei Wang (Dept. of Chem., Peking Medical Coll.). *Acta Chim. Sinica*, 1958, **24** (1), 42–46.—5-Aminothiazoline-2-thiocarboxyamide (**I**) may be used as a reagent for Pd^{2+}. As little as 0·003 μg of Pd (concn. limit, 1 in 1×10^6) can be detected when a spot test is carried out on paper with neutral or weakly acidic soln. Among 34 cations examined, Cu^{2+}, Pt^{4+}, Fe^{3+}, Ag^+, Au^{3+} and Hg^{2+} interfered. If a paper-chromatographic method is used, Pd^{2+} may be detected in the presence of considerable amounts of these ions. The formation of colour and ppt. between Pd^{2+} and **I** depends on acidity: *e.g.*, pH 1, brownish-red ppt.; pH 3 to 5, orange-red soln.; pH 5, orange-yellow turbidity; pH 6 to 8, turmeric-yellow ppt.; and pH >9, yellow soln. The extinction at pH 4 obeys the Beer-Lambert law in the range of 0·3 to 0·8 mg of Pd per 10 ml of soln. The colour is stable from 5 to 30 min. For a gravimetric determination, Pd^{2+} may be pptd. with **I** in ammoniacal soln. The ppt. is ignited to metallic Pd and weighed.

S. H. YUEN

4146. **EDTA titration of palladium.** J. Kinnunen and B. Merikanto (Outokumpu Oy, Metalworks, Pori, Finland). *Chemist Analyst*, 1958, **47** (1), 11.—*Procedure in ammoniacal soln.*—To a slightly acid soln. containing 5 to 50 mg of Pd add excess ($\simeq$ 30 ml) of 0·01 *M* EDTA. Dilute to 150 ml with ice-cold water, cool to 5°, add 0·1 g of ascorbic acid, a few drops of Eriochrome black T indicator, and ammoniacal buffer till the soln. becomes blue. Immediately back-titrate the excess of EDTA with 0·01 *M* $MnSO_4$ to a red end-point. *In acid soln.*—To the acid soln. (5 to 50 mg of Pd) add excess of 0·01 *M* EDTA and ammonium acetate till the pH reaches 3. Add a few drops of xylenol orange

indicator, titrate with 0·01 *M* $Th(NO_3)_4$ to red, then back-titrate with EDTA to yellow. The titration can also be carried out with $Tl(NO_3)_3$ in hot soln. at a pH of 4 to 5, and in the presence of other platinum-group metals. Thus, in the analysis of two samples of platinic ammonium chloride, 13·63% of Pd was found by the first procedure, compared with 13·71% by the dimethylglyoxime method, and, by the second procedure, 9·63%, as compared with 9·77 and 9·82% by dimethylglyoxime. R. E. ESSERY

4147. **Diallyldithiocarbamidohydrazine [di(allylthiocarbamyl)hydrazine] (Dalzin) as an analytical reagent: colorimetric determination of palladium.** N. K. Dutt and K. P. Sen Sarma (Univ. Coll. Sci., Calcutta). *Sci. & Cult.*, 1957, **23** (5), 249.—Palladium forms an orange-coloured complex with this reagent which is extractable by $CHCl_3$. The max. absorption is at 365 mμ at pH 1·2 to 2·6. Beer's law is obeyed with 0·4 to 2·0 μg of Pd. N. E.

4148. **Chemical analyses of minerals.** M. H. Hey (Dept. of Mineral., British Museum, London). *Miner. Mag.*, 1954, **30**, 481–497.—A detailed discussion is presented of the errors in chemical analyses and in the physical data which together enable the empirical unit-cell contents to be calculated, suggesting a probable formula. It is concluded that it is desirable to carry out all calculations to at least one place beyond the first significant figure liable to be affected by known sources of error, and to take care that the mathematical instruments (tables or slide-rules) used are adequate to this task. It is also usually desirable to estimate the accuracy of the several measurements made, and to calculate the effect on the final results of the several assessed errors. R. A. HOWIE

4149. **Analysis of dolomites, ankerites and magnesites in the presence of larger amounts of manganese.** M. Kvapil (Res. Inst. Ores, Prague). *Rudy*, 1957, **5** (12 Add.), 4–6.—When the residue after ignition and SiO_2 have been determined, R_2O_3 is pptd. with hexamine. Manganese in the filtrate can be pptd. with diethyldithiocarbamate and extracted with $CHCl_3$ or masked with triethanolamine; Ca and Mg can then be determined complexometrically, with the use of Fluorexone (fluorescein complexone) as indicator. *Procedure for Ca*—Dilute 50 ml (≡ 100 mg of the sample) of the filtrate (after separation of the R_2O_3) to 200 ml with water, add triethanolamine (25% soln.) (5 ml), 4 *N* NaOH (8 ml), KCN soln. (10%) (5 ml) and Fluorexone indicator and titrate with 0·05 *M* EDTA (disodium salt) in daylight. At the end-point the yellowish-green fluorescence is discharged and the soln. becomes pink. J. ZÝKA

4150. **Rapid analysis of some silicate materials.** H. Bennett, W. G. Hawley and R. P. Eardley (Brit. Ceram. Res. Ass.). *Trans. Brit. Ceram. Soc.*, 1958, **57** (1), 1–28.—Full details are given of methods applicable to materials which are completely decomposed either by HF - H_2SO_4 or by fusion with NaOH. Some of the conventional methods are modified. (*i*) In the determination of SiO_2 as the molybdosilicate complex (*cf.* Armand and Berthoux, *Anal. Chim. Acta*, 1953, **8**, 510), it is recommended that for material containing > 65% of SiO_2 only 0·25-g samples should be used; that the ppt. should not be allowed to run dry during filtration and washing; and that the ammonium molybdate soln. should not be more than 4 weeks old. (*ii*) The determination of Al_2O_3 as the 8-hydroxyquinoline complex is not suitable for materials having high SiO_2 to Al_2O_3 ratios, *e.g.*, silica bricks, sand. (*iii*) For Fe_2O_3 and TiO_2, colorimetric determinations on aliquots of the soln. of the fused sample are recommended. (*iv*) For the determination of CaO and MgO, complexometric titrations are recommended, with appropriate indicators, Al_2O_3, Fe_2O_3 and TiO_2 being sequestered with triethanolamine. (*v*) The alkali-metal oxides are determined by flame photometry. J. A. SUGDEN

4151. **Spectrographic analysis of some minor constituents in refractories.** D. D. Innes (Pilkington Brothers Ltd., St. Helens, Lancs., England). *Trans. Brit. Ceram. Soc.*, 1958, **57** (1), 29–37.—For Na_2O and K_2O, 0·05 g of sample is mixed with an equal wt. of an internal standard mixture of carbon powder containing 1% of RbCl, and is excited for 3·5 min. with 10 amp. d.c. in a hollow cathode. The line pairs used are K 7699·0 (0·05 to 5·0%) and Na 5895·9 (0·01 to 0·5%) - Rb 7947·6 A. For Fe_2O_3, TiO_2, CaO, MgO, ZrO_2 and Al_2O_3, 0·02 g of sample is mixed with 0·02 g of $SrCl_2$ and 0·08 g of an internal standard mixture of carbon powder containing 2·5% of Co_2O_3. The line pairs used are Fe 3021·1, Ti 3242·0, Ca 3179·3, Mg 2802·7, Zr 3392·0, Al 2652·2 - Co 2989·6 A. J. A. SUGDEN

4152. **Spectrochemical analysis of Portland cement and its raw materials.** D. Lesar. *S. Afr. Ind. Chem.*, 1957, **11** (11), 236–245.—Spectrophotometry is used for the determination of Si, Fe, Al and SO_4^{2-}, and, by the addition of a titration attachment, Ca and Mg can be determined complexometrically. Flame photometry is used for the determination of Na and K. Results are as accurate as those by classical procedures, but are obtained in about a quarter of the time. A. M. SPRATT

See also Abstracts—**3962**, Scheme for qual. analysis of the HCl group. **3971**, Oxidation-reduction volumetric reagents. **3973**, Use of chemiluminescent indicators for determination of Cr^{III}. **3978**, Ion exchange in inorganic analysis. **3981**, Use of catechol in photometric analysis. **4216**, Decomposition of pyrites in coal. **4308**, Determination of starch used in flotation. **4309**, Detection of ortho-, pyro- and poly-phosphates. **4391**, Determination of arsenite. **4192**, Stability of $Fe(SCN)_3$ in various media. **4228**, Determination of Hg. **4229**, Micro-determination of Tl. **4354**, Effect of porcelain crucibles on Cu determination. **4385**, Polarography of metal ions in fused LiCl - KCl.

3.—ORGANIC ANALYSIS

4153. **Use of dielectric-constant measurements in organic analysis.** S. B. Nagy (Res. Inst. for Ind. of Org. Chem. and Synthetic Resins). *Magyar Kém. Lapja*, 1958, **13** (2), 42–44.—Methods of measurement and their application to research on organic structure and the analysis of binary solvent systems are reviewed. The determination of organic compounds in aq. soln. is difficult because the electrolytic dissociation of trace impurities affects the dielectric constant. (26 references.) G. SZABO

4154. **New catalysts for carbon and hydrogen analyses.** T. S. West (Univ., Birmingham). *Chem. Age*, 1958, **79**, 396.—A review of recent papers.

4155. **Micro-determination of carbon and hydrogen in pyrophoric and hygroscopic organic compounds.** W. P. Pickhardt, L. W. Safranski and J. Mitchell, jun. (E. I. du Pont de Nemours and Co. Inc., Wilmington, Del.). *Anal. Chem.*, 1958, **30** (7), 1298–1301.—Polyethylene bags provide a simple and convenient means for protecting the sample from the atmosphere during sampling, weighing and transferring to the combustion tube in the analysis for C and H by the dry combustion method. The accuracy and precision are about the same as those attained by the conventional Pregl method.
G. P. Cook

4156. **Iodimetric micro- and ultra-micro determination of carbon and hydrogen. The determination of the carbon to hydrogen ratio without weighing.** J. Unterzaucher (Farbenfabrik Bayer A.-G., Leverkusen, Germany). *Mikrochim. Acta*, 1957, (3–4), 448–468.—The substance is burnt in a current of air over CuO. The excess of O carried along with the CO_2 and H_2O is separated by copper heated to $\simeq 600°$. The H_2O is removed by freezing at $\simeq -70°$ while the CO_2 is converted by carbon at 1120° into CO, which is absorbed by I_2O_5 and the liberated iodine titrated, giving the carbon content. The H_2O is now vaporised, passed over the heated carbon and the CO formed is determined in the same way, giving the hydrogen content. The liberated iodine in each case is converted into iodate and titrated with $Na_2S_2O_3$ soln. in the presence of KI and HCl in the usual way. The accuracy for a 3 to 4-mg sample is $\pm$ 0·1% absolute for C and $\pm$ 0·04% absolute for H. The C to H ratio may thus be determined without weighing the sample or standardising the $Na_2S_2O_3$ soln.
L. S. Adler

4157. **Mercurimetric determination of chlorine and bromine in organic compounds.** R. D. Glukhovskaya. *Trudy Tomsk. Univ.*, 1957, **145**, 77–82; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,628.—The method may be used for determining the halogens in DDT, dichlorobenzene, trichloroaniline, hexachlorobenzene, tribromobenzene, dibromobenzene, bromocamphor, $CHCl_3$ and CCl_4. Heat to redness 80 to 100 mg of substance with a small piece of metallic potassium (250 to 300 mg) in a closed dry bomb-tube for 15 to 20 min. Cool and open the tube, add absolute ethanol to dissolve unchanged potassium and transfer the ethanolic halide soln. to a beaker, rinsing out the tube with water. Neutralise the resulting cloudy soln., containing particles of C, with 6 *N* HNO_3 to phenolphthalein, filter and make the filtrate up to 100 ml. Acidify 10 ml with three drops of 0·5 *N* HNO_3, boil for 1 or 2 min. to remove CO_2, cool, add three drops of an ethanolic soln. of diphenylcarbazone and titrate with $Hg(NO_3)_2$ soln. to a violet colour. The method is simpler, takes less time and gives more accurate results than Volhard's method.
C. D. Kopkin

4158. **Experimental appraisal of methods of micro-determination of organic iodine.** A. Konovalov (Lab. de Chimie Générale, Louvain). *Ind. Chim. Belge*, 1958, **23** (1), 19–34.—Various known methods are compared and modifications to the methods of Grote and Krekeler (*Angew. Chem.*, 1933, **46**, 106) and Schöniger (*Anal. Abstr.*, 1957, **4**, 124) are suggested. (10 references.)
S.C.I. Abstr.

4159. **Specific detection of nitrogen through pyrolytic oxidation in organic spot-test analysis.** F. Feigl and J. R. Amaral (Min. de Agric., Rio de Janeiro, Brazil). *Anal. Chem.*, 1958, **30** (6), 1148–1150.—After an outline of the disadvantages of conventional methods for detecting N in organic spot-test analysis, the chemistry of the pyrolytic oxidation of N-containing compounds with manganese dioxide or manganic oxide to give HNO_2 is considered. Tests on 150 non-volatile nitrogenous compounds of all types have shown that the reaction provides a reliable method for demonstrating the presence of N, and a spot-test procedure in which HNO_2 is detected by the Griess nitrite reaction is described. Less than 0·5 mg of sample is placed in a micro test-tube, which projects through a perforated asbestos sheet, and intimately mixed with 0·3 g of manganese dioxide or manganic oxide. The mouth of the test-tube is covered with a filter-paper moistened with Griess reagent and the development of a pink circle on the paper when the bottom of the tube is heated rapidly indicates N. The limit of detection is 0·02 to 0·03 μg, and the procedure may be completed in 1 to 2 min. The presence of N in volatile compounds can also be demonstrated if loss of undecomposed volatile matter is prevented by heating the tube from the top instead of the bottom.
S. M. Marsh

4160. **The use of tritium bremsstrahlung for the determination of sulphur in hydrocarbons.** M. M. Kannuna and J. F. Cameron (Isotope Div., A.E.R.E., Harwell, England). *Intern. J. Appl. Radiation Isotopes*, 1957, **2** (1), 76–79.—An apparatus is described in which a sample is placed between a source of 114 mC of ^3H on an area of 1·3 sq. cm and a Geiger-Müller tube. For concn. up to at least 5% w/w of thiophen in benzene the reduction in count rate is directly related to concn. The sensitivity compares well with that of other X-ray and chemical methods.
G. J. Hunter

4161. **Spectroscopic detection of silicon in organic silicon compounds.** J. Radell, P. D. Hunt, E. C. Murray and W. D. Burrows (Aeronautical Res. Lab. of Wright Air Development Centre, Ohio, U.S.A.). *Anal. Chem.*, 1958, **30** (7), 1280–1281.—The qual. or semi-quant. method described is carried out on the Todd Spectranal by the use of the emission lines at 6347 and 6371 A. The sample is decomposed in acid solution by a spark discharge between platinum electrodes.
K. A. Proctor

4162. **Determination of mercury in organic compounds. A micro- and semi-micro method.** B. C. Southworth, J. H. Hodecker and K. D. Fleischer (Sterling-Winthrop Res. Inst., Rensselaer, N.Y.). *Anal. Chem.*, 1958, **30** (6), 1152–1153.—Mercury in organic compounds (*e.g.*, diuretics) may be determined by burning a sample in a flask containing conc. HNO_3 and filled with oxygen, when all the mercury becomes fixed as Hg^{2+}. The acid soln. is then adjusted to pH 7·5 with NaOH soln., and sufficient Na acetate to give a 0·2 *M* final soln. is added as pH 2·0 is reached. Mercury is then titrated amperometrically with either 0·01 or 0·001 *N* EDTA at zero applied potential *vs.* the S.C.E. Results for several compounds are tabulated and the accuracy compares favourably with that of other methods.
S. M. Marsh

4163. **Selective micro-determination of alkoxyl groups by gas - liquid chromatography.** — Vertalier and — Martin (Soc. des Usines Chim. Rhône-Poulenc, Rech. Anal., Vitry-sur-Seine, France). *Chim. Anal.*, 1958, **40** (3), 80–86.—An apparatus and its manipulation are described in which the alkoxyl compounds are converted into alkyl iodides by the Zeisel method, the iodides are distilled, transferred to a column containing octyl phthalate and Celite (1:2) and resolved, by means of a thermal-conductivity recorder, at 100° in a current of N at the rate of 1 litre per hour. The iodides are characterised by peaks on the curve, and retention times are given for methyl, ethyl, *iso*propyl, propyl, *iso*butyl and butyl iodides. As little as 0·01 mg of methyl iodide and 0·05 mg of butyl iodide can be identified in any compound, in 10 min. after distillation of the iodides, operating on 0·1 to 0·5 mg of sample. The procedure involves losses of 25 to 50%, and does not permit of determination, which, however, can be done by determining total alkoxyl groups by classical iodimetry, then referring the areas under the peaks of the curve to a standard curve relating, *e.g.*, the molecular ratio $-OCH_3$ to $-OC_2H_5$ to the peak ratio CH_3I to C_2H_5I, with 15 to 30 mg of sample, dissolving the iodides in 0·2 ml of $CHCl_3$, and operating on 0·01 ml of this soln. The determination of methoxyl and ethoxyl groups is carried out on 20 mg of sample, receiving the iodides in 0·2 ml of $CHCl_3$ containing 5% (v/v) of dichloromethane as internal standard, which gives a peak between those for methyl and ethyl iodides. The ratios of the peaks CH_3I to CH_2Cl_2 and C_2H_5I to CH_2Cl_2 are referred to standard curves obtained with known concn. by vol. of the two iodides, and calculated back to weight. The determination occupies 1·5 hr. With micro samples, errors are of the order of 5 to 10%, but with 20-mg samples the error is < 5%. Results are quoted for amino-methoxyquinoline and phenacetin, alone and in mixtures. R. E. Essery

4164. **Spectrophotometric assay for sulphydryl [thiol] groups using N-ethylmaleimide.** N. M. Alexander (Radioisotope Service, Veterans Admin. Hosp., West Haven, Conn.). *Anal. Chem.*, 1958, **30** (7), 1292–1294.—Thiol-containing soln. having a concn. as low as 0·0001 *M* can be determined by the method described, which has been applied successfully to the determination of total thiol groups in tissue extracts and whole blood. K. A. Proctor

4165. **Spectrophotometric assay for reaction of N-ethylmaleimide with sulphydryl [thiol] groups.** E. Roberts and G. Rouser (Dept. of Biochem., City of Hope Med. Center, Duarte, Calif.). *Anal. Chem.*, 1958, **30** (7), 1291–1292.—In soln. at pH 6 the absorption of N-ethylmaleimide at 300 mμ is diminished in proportion to the reaction with thiol groups and this can be used to determine the latter. Purines, pyridines and nucleosides do not interfere. K. A. Proctor

4166. **The infra-red spectra of *n*-paraffin hydrocarbons.** R. N. Jones. *Bull. Nat. Res. Council, Ottawa*, 1957, (5), 32 pp.—The i.r. absorption curves of seventeen *n*-paraffin hydrocarbons from *n*-hexane to *n*-hexatriacontane are illustrated. In a separate series of curves the spectra between 1480 and 1430 cm^{-1} are reproduced on an extended scale to demonstrate the appearance of additional absorption in the higher members of the series. [*Cf. Anal. Abstr.*, 1958, **5**, 3773). N. E.

4167. **Composition of Ilosvay's reagent used for the determination of acetylene in liquid oxygen.** Eizo Yasui and Hiroshi Suzuki (Res. Lab., Nagoya Plant, Toa Gosei Chem. Ind., Minato-ku). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1958, **61** (2), 173–176.—The absorption spectrum of Ilosvay's reagent containing various amounts of aq. NH_3 (< 2 *M*) and hydroxylamine hydrochloride soln. (**I**) (< 0·5 *M*) was examined. In the presence of a large excess of aq. NH_3 over **I**, a dense blue colour appears, owing to the oxidation of Cu with O. In the presence of an excess of **I** a yellowish-green ppt. appears. The colour of the reagent in the presence of acetylene changes in the sequence orange, red, violet and blue with increasing ratio of **I** to aq. NH_3. The best composition (for 250 ml) is as follows—$CuSO_4$ soln., 10%, 25 ml; aq. NH_3 soln. (sp. gr. 0·88, 1 + 1, by vol.), 20 ml; **I**, 30%, 25 ml; gelatin soln., 1%, 62·5 ml; anti-foaming agent (1% soln.), 18·8 ml. The absorption is measured at 517 mμ. The working curve is linear for < 10 p.p.m. (rate of flow 160 cu. cm per min., for 10 min.) (for the procedure see Matsui *et al.*, *Anal. Abstr.*, 1958, **5**, 554). For smaller amounts of acetylene, Geissman's formulation is preferred [$CuSO_4$ soln., 20%, 10 ml; **I**, 30%, 60 ml; aq. NH_3 (1:1), 30 ml; gelatin soln., 1%, 50 ml; water, 50 ml] (absorption at 562 mμ) (*Ind. Eng. Chem., Anal. Ed.*, 1947, **19**, 919). K. Saito

4168. **Mass-spectrum analysis of a mixture containing tetrachloroethane, trichloroethylene and the isomers of dichloroethylene.** S. E. Kupriyanov, R. V. Dzhagatspanyan and V. K. Potapov. *Khim. Prom.*, 1957, (5), 274–277; *Ref. Zhur., Khim.*, 1958, Abstr. No. 35,948.—Analytical details together with a method of interpreting and calculating the results are described. It is shown that with a three-component mixture it is possible to determine even 1 to 2% of a constituent with satisfactory accuracy. The maximum error for binary mixtures was 2·9% (abs.) and for ternary mixtures 1·5% (abs.). W. Roubo

4169. **Alkaline bromine as volumetric reagent, analytical applications. II. Estimation of *iso*propyl alcohol and acetone singly as well as in mixture.** K. C. Grover and R. C. Mehrotra (Chem. Lab., Univ. Lucknow, India). *Z. anal. Chem.*, 1958, **160** (4), 274–276 (in English).—Alkaline hypobromite soln. quant. oxidises acetone (**I**) to acetic acid and CO_2 in 10 min. at room temp. and *iso*propyl alcohol (**II**) to the same products in 1 hr. at b.p., and the reagent may be used for the volumetric determination of **I** and **II**. Since it is known that **II** can be determined by quant. oxidation to **I** with *N* $K_2Cr_2O_7$ in H_2SO_4 soln., a method is available for the individual determinations of **I** and **II** when present together. A. R. Rogers

4170. **Analysis of polymethylols. Quantitative determination of 2:2:6:6-tetra(hydroxymethyl)--*cyclo*hexanone and -*cyclo*hexanol.** L. Kamphenkel and G. von Hintzenstern (Inst. für Chemie u. Technol. der Plaste, Leipzig). *Chem. Tech., Berlin*, 1957, **9** (12), 704–710.—The condensation of *cyclo*hexanone and formaldehyde, and subsequent reactions, yield principally 2:2:6:6-tetra(hydroxymethyl)-*cyclo*hexanone (**I**) and -*cyclo*hexanol (**II**), and by-products. The reaction product is analysed completely, to permit determination of the alcohol and ketone. For the **II**, an amount of sample containing about 25 mg of the **II** is dissolved in water with addition of 3 ml of Hehner dichromate

soln. and 25 ml of 25% H_2SO_4; the mixture is kept at 95° to 100° for 4 hr. then 40 to 50 ml of 0·1 *N* Na_2AsO_3 is added to the cooled soln., with subsequent back-titration at 60° to 80° with 0·1 *N* $KBrO_3$, with methyl orange as indicator. **II** (%) is given by $a/(73{\cdot}42\ E - [K_1 + K_2 + K_7 + K_9])$ where E is sample wt., a is the titre (ml) and the K values are corrections (constant × content) for by-products, *viz*, K_1 for **I** 0·94198, K_2 for formaldehyde 0·97807, K_7 for *cyclo*hexanone 0·4486, and K_9 for formic acid 0·31904. For the determination of **I**, to a sample containing 25 mg of **I** are added 50 ml of KI - KIO_3 soln. and 20 ml of 10% KOH soln. and the mixture is set aside for 4 to 6 hr. followed by the addition of 10 ml of 25% H_2SO_4 soln. and titration of liberated iodine with $Na_2S_2O_3$ soln. **I** (%) is given by $b/(136{\cdot}4\ E - [K_3 + K_4])$, where K_3 (for formaldehyde) is 0·90724 and K_4 (*cyclo*hexanone) 1·1103. For the determination of formic acid, the aq. soln. (E ml) is steam-distilled at × 130° after addition of 50 ml of 50% H_3PO_4 soln. and the distillate is titrated with 0·1 *N* NaOH soln. The formic acid (%) is given by $d/460{\cdot}24\ E$. For the determination of *cyclo*hexanone, the method of Krause is used (*Pharm. Zentralh.*, 1951, **90**, 218), whence *cyclo*hexanone (%) is given by $f/[(907{\cdot}4 \times E) - K_4]$ and K_4 is the formaldehyde constant 32·685. For the determination of formaldehyde, the dimedone method of Vorlander is used (*Z. anal. Chem.*, 1927, **77**, 241), whence formaldehyde (%) is given by $c/300{\cdot}26\ E$ in the final titration. Methods of a conventional nature are also given for Na_2CO_3, $Ca(OH)_2$, $CaCO_3$, H_2SO_4, $CaSO_4$ and ash contents.

J. L. PROSSER

4171. **Salting-out chromatography. III. Aliphatic and polyglycol ethers, carboxylic acids.** R. Sargent and W. Rieman, III (Rutgers Univ., New Brunswick, N.J., U.S.A.). *Anal. Chim. Acta*, 1958, **8** (3), 197–203.—Distribution ratios and salting-out constants are determined for 16 ethers and glycol ethers on elution with $(NH_4)_2SO_4$ soln. from Dowex 50-X4 anion-exchange resin. These data are used to calculate the conditions necessary for the separation of mixtures of the ethers containing up to seven components. Carboxylic acids can also be separated by salting-out chromatography, but less successfully than by ion-exchange chromatography. (*Cf. J. Phys. Chem.*, 1957, **61**, 354; *Anal. Abstr.*, 1958, **5**, 2246.)

W. C. JOHNSON

4172. **Material deposited along path of chromatographed sugar spot.** C. K. Hordis and G. N. Kowkabany (Catholic Univ. of America, Washington, D.C.). *Anal. Chem.*, 1958, **30** (7), 1210–1213.—The amount of material distributed along the path of a sugar spot chromatographed on paper was determined with a ^{14}C tracer. Some of the material along the path of the spot appears to be the sugar originally chromatographed and it is in excess of the amount predicted by a Gaussian distribution. This may be due to the adsorptive forces of the paper competing with the liquid - liquid distribution. Approximately 0·5% of the material appears to be lost either preceding or following the spot.

G. P. COOK

4173. **Solvent for the paper-chromatographic separation of glucose and sorbitol.** W. R. Rees and T. Reynolds (Res. Inst. of Plant Physiol., Imp. Coll. of Sci. and Tech., London). *Nature*, 1958, **181**, 767–768.—Glucose and sorbitol can be separated in 7 hr. with ethyl methyl ketone, glacial acetic acid and saturated aq. boric acid soln. (9:1:1), with Whatman No. 54 paper, by the descending method.

G. S. ROBERTS

4174. **Acidity of sprays used in detecting ketohexoses on paper chromatograms.** R. W. Bailey (Plant Chemistry Div., D.S.I.R., Palmerston North, New Zealand). *Nature*, 1958, **181**, 836.—Indol-3-ylacetic acid in trichloroacetic acid as described by Heyrovský (*Biochim. Biophys. Acta*, 1956, **21**, 180) failed to detect those disaccharides that require prolonged hydrolysis. Their presence was revealed by replacement of trichloroacetic acid with 2 *N* HCl.

S. BAAR

4175. **Urea phosphate reagent as a specific test for heptoses on paper chromatograms.** F. L. Greene (Philip Morris Inc., Richmond, Va., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1164.—A specific test for identifying heptoses consists in dipping the paper chromatogram in a soln. of 1 g of urea and 4·5 ml of 85% H_3PO_4 in 48 ml of water-saturated *n*-butanol and heating at 105° for a few minutes. A distinctive pink colour is given by heptoses, but by none of the other carbohydrates tested. The range of detection is approx. 20 to 100 μg.

S. M. MARSH

4176. **Gradient elution of disaccharides on a stearic acid-treated charcoal column.** N. Hoban and J. W. White, jun. (E. Reg. Res. Lab., Philadelphia, Pa.). *Anal. Chem.*, 1958, **30** (7), 1294–1296.—The separation of four pairs of sugars—turanose - sucrose, isomaltose - gentiobiose, maltulose - nigerose, and melibiose - lactose, is described. A gradient from 0 to ≃ 7% of ethanol in H_2O was produced over a range of 140 fractions and the sugar content of selected fractions was determined colorimetrically with anthrone reagent to an accuracy of ≃ ± 5%. Individual sugars could not be identified by their peak eluate volume, but the relative order of elution was always the same. Four other pairs of sugars, although separable on paper, were also separated by this procedure.

G. P. COOK

4177. **Polarographic determination of hydrogen peroxide, formaldehyde and acetaldehyde in mixtures.** S. Sandler and Yu-Ho Chung (Univ. Toronto, Ontario, Canada). *Anal. Chem.*, 1958, **30** (7), 1252–1255.—Electrolytes, buffered at two different pH values, are used in the determination of the individual substances in three separate polarograms. Aldehydes do not interfere in the determination of H_2O_2 in an acid buffer soln. (pH 4·5). Formaldehyde is determined in an alkaline soln. (pH 12·2) to which $TiCl_4$ is added to eliminate interference by H_2O_2. Acetaldehyde is determined in a similar soln. to which dimedone is added to eliminate interference by formaldehyde. The H_2O_2, formaldehyde and acetaldehyde determinations are accurate to within ≃ ± 6%, ≃ ± 4% and ≃ ± 5%, respectively.

G. P. COOK

4178. **Volumetric determination of aldehydes, ketones and quinones.** A. Berka (Inst. Anal. Chem., Charles' Univ., Prague). *Chemie, Prague*, 1957, **9** (4), 528–539.—A review, with 63 references.

J. ZÝKA

4179. **Salting-out chromatography. IV. Aldehydes and ketones.** A. Breyer and W. Rieman, III (Rutgers Univ., New Brunswick, N.J., U.S.A.). *Anal. Chim. Acta*, 1958, **18** (3), 204–213.—With

the use of $(NH_4)_2SO_4$ soln. and Dowex and Amberlite resins, distribution ratios and salting-out constants are determined for thirteen ketones and four aldehydes. The effects of sample size, flow rate and particle size and cross-linking of the resin are studied, and the method is used for the separation of mixtures containing up to seven components. (*Cf. Anal. Abstr.*, 1958, **5**, 4171.)

W. C. JOHNSON

4180. **Quantitative determination of organic acids by partition paper chromatography.** Kh. U. Usmanov, A. M. Yakubov and A. B. Kuchkarev. *Trudy Sredneaz. Politekh. Inst.*, 1957, (2), 3–9; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,634.—A quant. determination of the components of a mixture of succinic, citric, tartaric, lactic and malonic acids in soln. of low concn. has been developed. Ascending chromatography is used, with *n*-butanol containing 5% of formic acid as solvent; the zones are revealed with a 0·04% ethanolic soln. of bromocresol green. The zones are cut out from the paper and the acids are extracted by boiling under reflux with twice-distilled water, and titrated with $Ba(OH)_2$ to phenolphthalein. The error of the determination is $\gtrless -6\%$. The abs. error of the determination in pure soln. of the acids is consistent by 0·015 to 0·080 mg, owing to adsorption of this amount of acid on the paper; this has been confirmed in special experiments.

C. D. KOPKIN

4181. **Determination of organic acids by partition chromatography on silica gel. II.** M. P. Pyatnitskiĭ and L. I. Kiprach. *Uch. Zap. Krasnodarsk. Gos. Ped. Inst.*, 1957, (19), 177–196; *Ref. Zhur., Khim.*, 1958, Abstr. No. 21,228.—The separation is carried out on a special column, with water cooling, of silica gel treated with 0·5 *N* H_2SO_4. The column is first washed with a mixture of butanol and $CHCl_3$ (1:4), which is also used as mobile phase. It is established that the use of a temp. within 5° to 25° does not influence the separation. For best results the silica gel should contain 8 to 9% of water and pass through a 100-mesh sieve. Mixtures of citric, oxalic, malonic and succinic acids are separated, and also mixtures of fumaric and succinic acids. Different samples of silica gel differ in their adsorption characteristics with respect to the acids. (*Cf. Anal. Abstr.*, 1958, **5**, 558.)

C. D. KOPKIN

4182. **Separation of halogenated acetic and propionic acids by paper chromatography.** J. W. Chittum, T. A. Gustin, R. L. McGuire and J. T. Sweeney (The College of Wooster, Ohio). *Anal. Chem.*, 1958, **30** (7), 1213–1214.—Good resolution of acetic, mono,- di- and tri-chloroacetic acids in mixtures of all four are achieved. Also, the bromo acids and acetic acids can be separated from each other. The developing solvent is *n*-butanol saturated with 1·5 *N* aq. NH_3. R_F values for 2- and 3-chloro- and bromo-propionic acids and 2:3-dibromo-propionic acid are included.

G. P. COOK

4183. **Stable 2-naphthol solution for fluorimetric determination of malic acid.** L. M. Sorensen and J. R. Matzke (Div. of Gerontology, Washington Univ., St. Louis, Mo., U.S.A.). *Chemist Analyst*, 1958, **47** (1), 20.—The stock 2-naphthol soln. (56 mg in 100 ml of 0·004 *M* NaOH) used for the determination of malic acid as a measure of fumarase activity becomes yellow and turbid after a few weeks, even under refrigeration. An aq. 2-naphthol soln. of the same concn., stored at 4° when not in use, gave 100% and 95% of its original fluorescence after storage for 100 and 655 days, respectively, when tested with known soln. of malic acid, and absorbance measurements at 320 mμ showed that 88% of the original 2-naphthol remained after 655 days. Solubility determinations at 3·5° and 27° gave figures of 26 and 67 mg per 100 ml of water, respectively, so that the stock soln. containing 56 mg per 100 ml must be made up at room temp., and warmed before use to ensure complete solution.

R. E. ESSERY

4184. **Chromatography of esters on Florisil. Detection as ferric hydroxamates.** F. B. O'Neal and J. Carlton (Georgia Inst. of Technol., Atlanta, Ga.). *Anal. Chem.*, 1958, **30** (6), 1051–1053.—The chromatographic behaviour of several homologous series of esters was studied with column packings of Florisil, silicic acid and alumina. The position of the adsorbed bands was indicated by formation of ferric hydroxamates. The column was first streaked with a filtered mixture (1:1) of hydroxylamine hydrochloride soln. (12·5 g in 100 ml of methanol) and NaOH soln. (12·5 g in 100 ml of methanol) and then, after being baked for 2 min. under an i.r. lamp giving a surface temperature of 135°, overstreaked with ferric perchlorate soln. (0·8 g of c.p. iron wire dissolved in 70% $HClO_4$ and made up to 100 ml with ethanol, 5 ml of soln. then being diluted with 1 ml of $HClO_4$). Purple zones indicated the adsorbed esters. The streaking reagent did not give reproducible results on silicic acid or alumina. Results obtained on Florisil columns for a series of ethyl esters up to ethyl decanoate indicated that the *R* values generally increased as the number of carbon atoms in the chain increased. *R* values for a short series of acetates showed a very regular increase with increase in the hydrocarbon chain of the alcoholic half of the molecule. Unsaturation in the aliphatic chain decreased the *R* value. The behaviour of some halogenated and branched-chain esters was also studied. The presence of chlorine atoms appears to reduce adsorption.

S. M. MARSH

4185. **Alkaline bromine as volumetric reagent, analytical applications. I. Estimation of ammonia, urea and thiourea.** K. C. Grover and R. C. Mehrotra (Chem. Lab., Univ. Lucknow, India). *Z. anal. Chem.*, 1958, **160** (4), 267–273 (in English).—Alkaline hypobromite soln. quant. oxidises NH_3 or urea to N and CO_2, and thiourea to N and H_2SO_4. Alkaline hypoiodite oxidises thiourea to urea and H_2SO_4, but does not oxidise NH_3 or urea. *Procedure*—Acidify 0·1 *N* bromate - bromide mixture (20 ml) with *N* H_2SO_4 (5 ml) in a 750-ml stoppered flask. After 10 min. at 40° add *N* NaOH (8 ml) and mix. The reagent contains about 67% of hypobromite, and a 50% or 100% excess must be used in the quant. determination of NH_3, urea or thiourea. Allow the reagent to stand with the sample (5 to 20 mg) at room temperature for 15 min. (for NH_3) or at the b.p. for 20 min. (for urea or thiourea), add 0·25 *N* KI (25 ml) and 2 *N* H_2SO_4 (25 ml) and titrate after 20 min. with 0·1 *N* $Na_2S_2O_3$. Perform a blank titration simultaneously.

A. R. ROGERS

4186. **Titration of weak bases in strong salt solution.** F. E. Critchfield and J. B. Johnson (Union Carbide Chem. Co., S. Charleston, W. Va.). *Anal. Chem.*, 1958, **30** (7), 1247–1249.—Weak bases such as aniline can be titrated potentiometrically

or with indicators in strong aq. soln. of neutral salts (6 to 8 *M*); these enhance the potentiometric break. Bases with ionisation constants of 1×10^{-12} can be titrated potentiometrically, whilst the indicator method is suitable for bases with constants of $> 1 \times 10^{-11}$. The method is also applicable to the titration of the individual amino nitrogens of polyfunctional amines and to the differentiation of bases in general. G. P. COOK

4187. **Sodium hypochlorite as a volumetric reagent. I. Determination of organic derivatives of hydrazine.** B. Singh, S. S. Sahota and S. Singh (Punjab Univ. Coll., Hoshiarpur, India). *Z. anal. Chem.*, 1958, **160** (6), 429–432 (in English).—Organic hydrazine derivatives can be titrated in 2 to 3·5 *N* HCl with NaOCl (0·1 *N*) in the presence of ICl and $CHCl_3$. The end-point is sharp and is indicated by the discharge of the iodine colour from the $CHCl_3$ layer. The NaOCl soln. is prepared by passing Cl into 0·4 *N* NaOH and standardising iodimetrically. G. BURGER

4188. **Potentiometric titration of free amine and amine carbonate in carbonated monoethanolamine solutions.** Yi-Chung Chang (Low-temperature Tar Lab., U.S. Bureau of Mines, Morgantown, W. Va.). *Anal. Chem.*, 1958, **30** (6), 1095–1097.—A reliable method for the determination of ethanolamine and its carbonate in soln. was required in connection with the regeneration of carbonated ethanolamine soln. used in a phenol-extraction process. The double-end-point potentiometric titration of such soln. with HCl was studied and found to give results within 2% of calculated figures, which is satisfactory for routine control analysis. The end-points occur at pH 7 and pH 4. Small amounts of phenol and other weakly acidic materials, *e.g.*, tar acids, do not interfere, but the presence of stronger acids, *e.g.*, sulphur dioxide, is likely to lead to errors. S. M. MARSH

4189. **Identification and quantitative analysis of certain quaternary ammonium compounds using ultra-violet absorption spectra.** M. Pernarowski and L. G. Chatten (Food and Drug Admin., Dept. of National Health and Welfare, Ottawa, Ontario, Canada). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (3), 211–214.—The u.v. absorption spectra of cetylpyridinium chloride, benzethonium chloride, dodecylacetamidodimethylbenzylammonium chloride and domiphen bromide in aq. soln. are reported. Spectrophotometric determinations of these compounds in pharmaceutical products gave good results in many cases. High concn. of dyes interfere with the quant. analysis, but it is still possible to identify the quaternary ammonium compound. A. R. ROGERS

4190. **Murexide test [for purines] in paper chromatography.** N. B. Chanda and S. Chakraborty (Tocklai Exp. Sta., Indian Tea Ass., Cinnamara, Assam). *Nature*, 1958, **181**, 836.—The papers are sprayed with 10% chloramine T, then with *N* HCl, heated in a steam oven, exposed to ammonia vapour and re-heated in the steam oven. The presence of purines in microgram quantities is indicated by pink spots. Uric acid, caffeine, theophylline, theobromine and xanthine can be detected by this method in amounts of 1·5, 18, 38, 1 and 7 μg, respectively. These minimum detectable amounts can be reduced if the spots are viewed in u.v. light, when a violet fluorescence is shown. S. BAAR

4191. **Polarographic study of cytotoxic nitrogen mustards.** R. Mantsavinos and J. E. Christian (Dept. of Pharm. Chem., Purdue Univ., W. Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1071–1073.—Pharmacologically active ethyleneimonium ions formed by the cyclisation of β-chloroethyl groups of aliphatic nitrogen mustards are reducible at the dropping-mercury electrode. The diffusion current obtained is linearly related to the concn. over certain ranges and the waves appear to be irreversible. Procedures are described for the quant. determination of intermediates and for determining the rate of the initial cyclisation. K. A. PROCTOR

4192. **Titration of thiols by the "STAS" method; the stability of ferric thiocyanate in various media.** M. Constantinescu and T. Constantinescu. *Lucr. Inst. Petrol Gaze Bucharest*, 1957, **3**, 353–363 (in Romanian).—The appreciable errors (up to 12%) in determining thiols, *e.g.*, in benzene, by pptn. as AgSH followed by titration of the excess of $AgNO_3$ with 0·05 *N* ammonium thiocyanate soln. (*cf.* Reid, *Ind. Eng. Chem., Anal. Ed.*, 1929, **1**, 186) are investigated quant. and discussed. The chief sources of error are the photolytic reactions, the decomposition of $Fe(SCN)_3$ in the presence of AgSH, and the occlusion of $AgNO_3$ and Ag_2O in the ppt. of AgSH. In the improved method, which is applicable to a wide range of thiol concn., an excess of $AgNO_3$ soln. containing $\simeq$ 4 ml of conc. HNO_3 per litre is added to the sample (50 ml), the suspension is shaken vigorously for $\simeq$ 5 min. in a stoppered flask, the ppt. is collected, and 10 ml of the filtrate is then titrated with a standard soln. of ammonium thiocyanate; 0·6 ml of ferric alum soln. (concn. not specified) is added as indicator. The presence of HNO_3 suppresses the formation of colloidal AgSH. W. J. BAKER

4193. **Polarography of thiourea.** C. J. Nyman and E. P. Parry (Dept. of Chem., State Coll. of Washington, Pullman, U.S.A.). *Anal. Chem.*, 1958, **30** (7), 1255–1257.—The determination of thiourea in neutral and acid soln. has been studied with respect to the formation constants of the complexes with mercury. K. A. PROCTOR

4194. **New methods for the quantitative determination of chlorine in organosilicon compounds.** L. V. Mȳshlyaeva. *Trudȳ Moskov. Khim.-Tekhnol. Inst. im. D. I. Mendeleev*, 1957, (25), 29–32; *Ref. Zhur., Khim.*, 1958, Abstr. No. 24,900.—Two methods are proposed for the determination of Cl directly linked to Si in certain alkyl- and aryl-chlorosilanes. The iodide - iodate method is based on the iodimetric determination of the HCl formed on hydrolysis of the chlorosilanes. Transfer the sample (0·1 to 0·25 g) to a flask containing 10% KI soln. (25 ml), 8% KIO_3 soln. (12 ml) and water (20 to 25 ml); after 5 or 7 min. titrate the liberated iodine with 0·05 *N* $Na_2S_2O_3$. The determination of Cl in alkoxychlorosilanes by this method gives low results. The aniline method is based on the quant. formation of aniline hydrochloride according to the equation—

$$R_nSiCl_{4-n} + 2(4-n)C_6H_5NH_2 = R_nSi(NHC_6H_5)_{4-n} + (4-n)C_6H_5NH_2.HCl.$$

Place the sample (0·1 to 0·25 g), in a glass ampoule, in a dried and weighed beaker with a porous bottom containing 7 to 10 ml of a mixture of anhyd. aniline with benzene or ether (1:4), break the ampoule and after 5 min. suck off the liquid and wash the ppt.

with benzene or ether. Dry the beaker with the ppt. of aniline hydrochloride to const. wt. at 105°. The method is not suitable for the analysis of alkoxychlorosilanes. C. D. KOPKIN

4195. **Determination of silanols with Grignard reagent.** F. O. Guenther (Gen. Electric Res. Lab., Schenectady, N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1118–1120.—The gasometric apparatus and procedure described is a modification of that used by Fuchs *et al.* (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 507). A soln. of the sample in di-*n*-butyl ether is added to a standard soln. of CH_3MgI (in the same solvent) in the reaction flask through which a slow stream of methane is passed. The vol. of gas collected is measured after $\simeq 6$ to 10 min.; the percentage of OH is calculated by a formula given. The method is applicable to the hydrolysis products from alkyl and aryl trialkoxysilanes as well as to commercial silicone resins. The abs. error, independent of gas vol., is $\pm$ 0·2 ml; about 12 analyses can be made in a day. For a sample of silicone resin, most of the solvent should be removed under vacuum at room temp. before dilution with di-*n*-butyl ether. W. J. BAKER

4196. **Polarographic determination of ethylmercury chloride and methoxyethylmercury chloride in binary mixtures.** Nao Shirota, Masato Kotakemori and Hisao Handa (Mishima Plant, Sankyo Co., Mishima, Shizuoka-ken). *Ann. Rep. Takamine Lab.*, 1957, **9**, 198–206.—In 0·1 *M* KNO_3 containing Britton - Robinson's buffer and 0·01% of gelatin, ethylmercury chloride (**I**) gives a two-step wave ($E_{\frac{1}{2}} = -0{\cdot}49$ V and $-1{\cdot}6$ V *vs.* the S.C.E.) at pH 1·9 to 11·8. The wave height is proportional to concn. for $< 3 \times 10^{-4}$ *M*, and is independent of the pH. In the same soln., methoxyethylmercury chloride (**II**) gives one wave ($E_{\frac{1}{2}} = -0{\cdot}49$ V) at pH $< 2{\cdot}9$, the height being proportional to concn. for $< 2{\cdot}5 \times 10^{-4}$ *M*. At pH > 8, **II** gives a two-step wave ($E_{\frac{1}{2}} = -0{\cdot}49$ V and $-1{\cdot}2$ V), the height of the first wave being proportional to concn., but almost one-half of that at pH 2·9. Since the law of addition holds for their wave heights at $-0{\cdot}49$ V, irrespective of the pH, a binary mixture can be analysed by the measurement of the wave height at pH 2·9 and 10·0, and by means of an empirical formula. The deviation is $\simeq 1{\cdot}5\%$. K. SAITO

4197. **Detection of polynuclear hydrocarbons and phenols with benzal [benzylidene] and piperonal [piperonylidene] chlorides.** E. Sawicki, R. R. Miller, T. Stanley and T. Hauser (Robert A. Taft Sanitary Engng Center, U.S. Public Health Service, Cincinnati 26, Ohio). *Anal. Chem.*, 1958, **30** (6), 1130–1133.—Sensitive colour tests for polynuclear aromatic hydrocarbons and phenols are described in which the compound is treated with benzylidene chloride (**I**) or piperonylidene chloride (**II**) in trifluoroacetic acid to give diarylmethane dyes which are then examined spectroscopically. (*a*) *Test with* **I**—A soln. of 50 to 5000 μg of the compound in 0·5 ml of $CHCl_3$ is treated with 5 ml of trifluoroacetic acid and 1 drop of **I**. After 5 min., 2 drops of H_2SO_4 are added and the colour is examined spectrophotometrically. In a more sensitive procedure, 1 ml of trifluoroacetic acid is added to a soln. of 5 to 60 μg of the compound in 0·1 ml of $CHCl_3$ followed by 0·005 ml of **I**. After 5 min., the mixture is diluted with 10 ml of H_2SO_4 and the absorption spectrum is determined. The colours, long-wavelength maxima and sensitivities of the test are tabulated for 39 phenols and hydrocarbons. (*b*) *Test with* **II**—To a soln. of 1 to 60 μg of the compound in 1 ml of $CHCl_3$ are added 5 ml of trifluoroacetic acid and 0·7 ml of 5% **II** in $CHCl_3$ (prep. described). After dilution with 10 ml of trifluoroacetic acid, the soln. is set aside for 5 to 10 min. and the absorption spectrum is determined. Alternative reagent soln. are suggested. The colour and long-wavelength maxima are given for the products from 51 polynuclear hydrocarbons and phenols. The reaction products of **II** usually absorb at a longer wavelength than do analogous products of **I**. The method has possible applications in the determination of phenols in air, of aromatics in air particulate matter and also in the fields of petroleum and cancer chemistry. S. M. MARSH

4198. **Solubilisation chromatography. I. Phenols and alcohols.** J. Sherma and W. Rieman, III (Rutgers Univ., New Brunswick, N.J., U.S.A.). *Anal. Chim. Acta*, 1958, **18** (3), 214–220.—Solutions of acetic acid (*N* to 6 *N*) are used as eluents for phenols and alcohols on ion-exchange (Dowex resin) columns. Values of *C*, the distribution ratio, are determined for five phenols and sixteen alcohols and the significance of the variation of log *C* with changes in the molarity of the acetic acid eluent is discussed. Four phenols and six alcohols, respectively, are separated by this method. W. C. JOHNSON

4199. **Separation of isomeric polyphenyls by adsorption chromatography.** M. Hellmann, R. L. Alexander, jun., and C. F. Coyle (Nat. Bureau of Standards, Washington, D.C.). *Anal. Chem.*, 1958, **30** (7), 1206–1210.—The chromatographic behaviour of selected polyphenyls was studied in order to develop a method for separating these compounds. A variety of adsorbents such as alumina, fuller's earth, silica gel and different grades of charcoal were used, and *iso*octane, *cyclo*hexane and $CHCl_3$ were used as eluents. The alumina - *iso*octane system gave max. efficiency in separation and recovery. Some charcoals gave better separation but poorer recovery. The polyphenyl content of the fractions was measured by spectrophotometric analysis. The results indicated that the separation of the polyphenyls follows a definite pattern, which can be correlated with the steric configuration of the molecule. G. P. COOK

4200. **Infra-red spectra of crystalline polyphenyls.** J. E. Stewart and M. Hellmann (Beckman Instruments, Inc., Fullerton, Calif., U.S.A.). *J. Res. Nat. Bur. Stand.*, 1958, **60** (2), 125–136.—The i.r. spectra (5 to 38 μ) of the solid phases of 16 polyphenyls ranging from diphenyl to *m*-octophenyl are listed, and the band frequencies and assignments are discussed fully in relation to the Randle - Whiffen assignments for substituted benzenes. There are two rotational isomers of *m*-quaterphenyl. W. J. BAKER

4201. **Gas - liquid partition chromatography of mixtures of aryl methyl ethers.** W. Carruthers, R. A. W. Johnstone and J. R. Plimmer (Carcinogenic Substances Res. Gp., The Univ., Exeter, England). *Chem. & Ind.*, 1958, (11), 331.—The authors give the retention volumes, relative to anisole, of three tolyl, six xylyl and two methoxyphenyl methyl ethers, at 145°, with a 260-cm column of Apiezon M grease and Celite (1:2·5) and N as carrier gas (14 ml per min.). Neither *m*- and *p*-tolyl nor 2:5- and 3:5-xylyl methyl ethers

could be separated under the conditions given. The method has been used to analyse the phenolic constituents of tobacco smoke. R. E. ESSERY

4202. **Separation and determination of aromatic acids by paper chromatography.** Z. Kh. Abidova, A. M. Yakubov, Kh. U. Usmanov and G. Kh. Khodzhaev. *Dokl. Akad. Nauk, UzSSR*, 1957, (6), 29–32; *Ref. Zhur., Khim.*, 1958, Abstr. No. 14,236.—Study is made of the separation of mixtures of benzene-1:2:4:5-tetracarboxylic, phthalic and *iso*-phthalic, benzoic and toluic acids on various types of paper and with various solvents. The best results are obtained with mixtures of *n*-butanol with aq. NH_3 (4:1), pyridine or saturated ammonium carbonate soln. With increase of the number of carboxylic groups in the molecule, the R_F value decreases. A clean separation of phthalic and *iso*-phthalic acids was obtained. To reveal the spots, a soln. of 50 mg of methyl red in 100 ml of ethanol is used. The chromatography is carried out by the ascending method for 12 to 15 hr.

C. D. KOPKIN

4203. **Piperonal [piperonylidene] chloride test for aromatic acylamines.** E. Sawicki (Robert A. Taft San. Engng Center, U.S. Dept. of Health, Education and Welfare, Cincinnati, Ohio, U.S.A.). *Chemist Analyst*, 1958, **47** (1), 9–11.—To 1 ml of a soln. of the test substance in $CHCl_3$ add 0·7 ml of a 5% soln. of piperonylidene chloride in $CHCl_3$ and dilute to 10 ml with trifluoroacetic acid. Shake till homogeneous, allow to stand for 5 to 10 min. and note the colour. The colours developed, with wavelength of maximum absorption, are listed for 41 compounds, for 27 of which are also given the sensitivities, expressed as μmoles per 3 ml giving an extinction of 0·1 in a 1-cm cell. The test is adversely affected by phenols and aromatic hydrocarbons, except benzene. The phenols are removed by alkaline extraction; the hydrocarbons are not usually found as contaminants in appreciable quantity. The test is applicable to the detection of the carcinogen N-2-fluorenylacetamide, and its 7- and 3-hydroxy metabolites, in dust and air. Preliminary work suggests that it can be used for the spectrophotometric determination of a large number of aromatic N-acylamines.

R. E. ESSERY

4204. **Determination of *p*-nitrophenacylamine hydrochloride.** Takeshi Kimura and Noribumi Sasaki (Shinagawa Plant., Sankyo Co. Shinagawa-ku, Tokyo). *Ann. Rep. Takamine Lab.*, 1956, **8**, 138–141.—*p*-Nitrophenacylamine hydrochloride (**I**) (an intermediate for the preparation of chloramphenicol) exhibits an absorption max. at 268 mμ in aq. soln., the extinction being proportional to concn. for 1 to 10 μg per ml. No interference results from NH_4Cl (the main impurity in crude **I**). K. SAITO

4205. **Determination of aromatic nitro compounds.** W. B. Koniecki and A. L. Linch (Med. Div. Ind. Hygiene Lab., E.I. du Pont de Nemours & Co., Penns Grove, N.J.). *Anal. Chem.*, 1958, **30** (6), 1134–1137.—The method described is particularly applicable to the analysis of urine when evaluating exposure to aromatic nitro compounds in manufacturing areas. The sample (5 ml) is treated with 10% Na_2CO_3 soln. (3 ml) and 20 to 25 mg of thiourea dioxide and maintained at 50° for 15 to 20 min. to reduce the nitro compounds to the corresponding amines. Excess of reagent is destroyed by heating at 50° after addition of 10% HCl (15 ml). The mixture is then diazotised and coupled with Chicago acid (0·5 g of 8-amino-1-naphthol-5:7-disulphonic acid dissolved in 1 ml of 37% HCl and diluted to 50 ml with water) to give a red azo dye. After the excess of nitrite has been destroyed by treatment with 10% sulphamic acid, the dye is estimated by light transmittance. The procedure is useful in the concn. range 10 to 150 μg but, beyond these limits, difficulties are encountered in the measurement of light absorption. Results are presented for a series of 18 aromatic nitro compounds and also for representative urine samples. Standard deviations of replicate determinations for the 18 compounds studied were within the range ± 5 μg. Precautions necessary to ensure the accuracy and reproducibility of the method are considered.

S. M. MARSH

4206. **Quantitative determination of camphor as its oxime.** A. Kolusheva and A. Morozova. *Farmatsiya, Bulgaria*, 1957, **7** (2), 27–31; *Ref. Zhur., Khim.*, 1958, Abstr. No. 14,248.—A method has been developed for the determination of camphor (**I**) in the pure form, and in alcoholic soln., and in camphor oil. Mix the sample (containing ≃0·2 g of **I**) with 5 ml of hydroxylamine hydrochloride soln. (8 g of hydroxylamine hydrochloride, 20 ml of water, 5 ml of pyridine, and 96% ethanol to 100 ml) and 2 drops of an ethanolic 0·1% soln. of bromophenol blue and boil for 4 hr. Cool, wash down the sides of the flask with 20 ml of ethanol, add 20 ml of water and titrate with 0·1 *N* HCl in the presence of 10 drops of bromophenol blue to a green colour. A blank is carried out simultaneously. The error in determining **I** in the pure state and in alcoholic soln. is ± 2%, and in camphor oil ± 5%. C. D. KOPKIN

4207. **Detection of triterpenoid acids on paper chromatograms.** B. Pasich (Dept. of Pharmacog., Pharm. Fac., Med. Acad., Poznań). *Nature*, 1958, **181**, 765.—Three methods of detection on alumina-impregnated filter-paper are described. (*i*) The air-dried paper is sprayed with an alcoholic soln. of tungstophosphoric acid (25%) and dried at 115° to 118° for 2 min. Spots made by as little as 3 to 5 μg of the acid component are then visible. (*ii*) The paper chromatogram is drawn through a 1% soln. of anhyd. $SnCl_4$ in pure thionyl chloride, and heated at 85° to 90° for approx. 1 min. (Noller's reaction). (*iii*) The paper is sprayed with a soln. of defibrinated goat's blood in normal saline (1:8). The triterpene acids appear as pale spots on a dark background.

G. S. ROBERTS

4208. **Indole and its derivatives. III. Quantitative determination of indole.** Shigeki Horiie (Inst. for Sci. and Technol., Osaka Univ., Sakai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (2), 225–227.—The determination of indole (**I**) was examined for application to the analysis of reaction mixtures containing aniline and acetylene. The orange-red colour given by **I** with HNO_2 obeys Beer's law for < 1 mg of **I** per ml. No similar coloration takes place with other ingredients, including aniline, quinoline, quinaldine, pyrrole, naphthalene, carbazole, diphenylamine, skatole and 5-methylindole. Congo red soln. is used as reference soln. The reaction mixture (2 g) is steam-distilled

with NaOH (≃1 g), and ≃100 ml of distillate is collected and made up to 100 ml. An aliquot is diluted to 50 ml after addition of conc. H_2SO_4 (0·5 ml) and $NaNO_2$ soln. (2%, 0·5 ml). The colour is compared with a standard series of Congo red soln. with a Duboscq colorimeter at 15°. The error is < 5%.

K. SAITO

4209. **Application of anhydro-titrimetry to the determination of benzotriazoles.** C. Hennart and E. Merlin (Orgasynthèse, Lab. de Vitry, Seine, France). *Chim. Anal.*, 1958, **40** (3), 87–88.—Benzotriazoles (≃ 1 millimole) are dissolved in 25 ml of dimethylformamide and titrated with 0·1 *N* K methoxide, to a pure blue end-point, with azo violet as indicator. The titrant is prepared by dissolving, under refrigeration, 4 g of potassium metal in a mixture of 100 ml of abs. methanol and 250 ml of anhyd. benzene, making up to 1 litre with benzene and standardising with acetic acid. The indicator is prepared from *p*-nitroaniline and resorcinol by the method of Meldola (*J. Chem. Soc.*, 1885, **47**, 657) and used as a 0·2% soln. in methanol - benzene (1 : 3). Titration curves are given for 0·144 g of benzotriazole and 0·128 g of 5-methylbenzotriazole.

R. E. ESSERY

4210. **Gas-chromatographic analysis of engine exhaust and atmosphere. Determination of C_2 to C_5 hydrocarbons.** F. T. Eggertsen and F. M. Nelsen (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1040–1043.—The hydrocarbons are first trapped in a short column cooled in a liquid-oxygen bath and then analysed by elution with helium through a longer column with thermal-conductivity detection. The components are determined planimetrically. The limit of detection is about 0·05 p.p.m.

K. A. PROCTOR

4211. **Determination of acids and basic nitrogen compounds in petroleum products.** I. Kukin (Gulf Research & Development Co., Pittsburgh, Pa.). *Anal. Chem.*, 1958, **30** (6), 1114–1117.—Non-aqueous titration procedures with visual indicators are suggested for the determination of acids and of weakly basic nitrogen compounds in petroleum products. Acids are determined by adding benzene - *iso*propyl alcohol (1 : 1) to a 20-g oil sample until the volume is 120 ml, then 5 drops of a 0·1% soln. of *p*-naphtholbenzein indicator in methanol, and titrating with 0·03 *N* alcoholic NaOH until the colour changes from orange to green. A special titration flask with a very narrow neck (*cf. Anal. Chem.*, 1957, **29**, 461) is used to facilitate the observation of colour change in dark oils. Comparison with ASTM methods indicates that the procedure is useful for dark oils and for those with acid values < 0·1. If weakly acidic zinc salts are present it is preferable to use an indicator with higher transition point. For the estimation of basic nitrogen compounds, benzene - glacial acetic acid (1 : 1) is added to a 20-g sample to a volume of 120 ml. After addition of 5 drops of 0·25% methyl violet in glacial acetic acid as indicator, the mixture is titrated with 0·08 *N* $HClO_4$. Comparison of results with those obtained by a potentiometric method indicates that the procedure is satisfactory. The indicator end-point can be determined to within 0·015 ml, even in the darkest oils.

S. M. MARSH

4212. **Polarographic estimation of thiophens and aromatic sulphides in petroleum.** H. V. Drushel and J. F. Miller (Mellon Inst. of Ind. Res., Pittsburgh, Pa.). *Anal. Chem.*, 1958, **30** (7), 1271–1280.—Various sulphones were synthesised from the parent sulphur compounds by oxidation with H_2O_2, and their polarographic behaviour was investigated. Sulphur concentrates of crude oils were separated into fractions of narrow mol.-wt. range by mol. distillation. The fractions were oxidised with H_2O_2 under controlled conditions and the resulting sulphones were polarographed. From a knowledge of the polarographic behaviour of the synthesised sulphones, the polarograms of the samples were interpreted and the percentages of thiophen S and aromatic sulphide S were calculated. This and the determination of aliphatic sulphides (*Anal. Abstr.*, 1955, **2**, 2480) accounted for at least 90% of the total S in most samples examined.

G. P. COOK

4213. **Aromatic types in a heavily cracked gas oil fraction. Combined use of ultra-violet and mass spectrometry.** R. J. Gordon, R. J. Moore and C. E. Muller (Martinez Res. Lab., Shell Oil Co., Emeryville, Calif.). *Anal. Chem.*, 1958, **30** (7), 1221–1224.—The use of low-electron-voltage mass spectra helps to avoid ambiguity in the determination of high-mol.-wt. aromatics by means of u.v. spectrophotometry and largely eliminates the spurious peaks frequently found in high-voltage conventional mass spectra. Trace amounts of tri- and tetranuclear compounds can be detected. The use of a heavily cracked gas oil as a source of secondary calibration materials appears promising in extending mass-spectral calibrations based on pure compounds to more complex natural aromatic petroleum fractions.

K. A. PROCTOR

4214. **Carbon-type composition of viscous fractions of petroleum. Density - refractivity intercept method.** S. S. Kurtz, jun., R. W. King, W. J. Stout and M. E. Peterkin (Sun Oil Co., Marcus Hook, Pa.). *Anal. Chem.*, 1958, **30** (7), 1224–1236.—The molecular vol. and density of saturated polycyclic and polycyclic aromatic hydrocarbons can be calculated with a standard deviation of ≃ ± 0·008. Differences of observed density due to differences in number or type of ring structures amount to several units in the second decimal place and therefore calculated densities can be used for evaluating C-type composition. The molecular vol. and density for all the basic structures having 15, 20, 26, 30 and 40 C atoms were calculated and a correlation between calculated density and refractivity intercept is given which derives the C-type composition for oils having between 15 and 40 C atoms, if the number of C atoms is known. This is obtained from an equation based on mol. wt. and a viscosity-gravity constant. The correlation can be used for all types of viscous petroleum oils. Good agreement with the results by the Kurtz - Martin method was obtained.

G. P. COOK

4215. **Potentiometric determination of sulphur in coal.** D. E. Galkin. *Trudy Tomsk. Univ.*, 1957, **145**, 67–68; *Ref. Zhur., Khim.*, 1958, Abstr. No. 17,587.—The method described is based on the non-compensation potentiometric titration of SO_4^{2-} with $Pb(NO_3)_2$ soln. after decomposition of the sample of coal by Eschka's method. To 50 ml of the soln. obtained from the sample add 0·1 *M* $K_3Fe(CN)_6$ (1 ml), 0·005 *M* $K_4Fe(CN)_6$ (0·1 ml,

3 drops) and an equal vol. of ethanol, and titrate with $Pb(NO_3)_2$ soln., with a bimetallic system of electrodes (platinum and silver). The error of the determination is $\pm$ 0·14%. The described method is more rapid than the gravimetric method.

C. D. KOPKIN

4216. **Decomposition of pyrites in coal by the action of dilute nitric acid.** E. I. Shmuk. *Izv. Akad. Nauk, SSSR, Otd. Tekh. Nauk*, 1957 (8), 126–128; *Ref. Zhur., Khim.*, 1958, Abstr. No. 21,203.—By the microscopic study of the oxidation products of pyrites in coal, it is established that one of the final products of the reaction between pyrites and dil. HNO_3 is elementary S. The formation of elementary S in coal, just as in pure pyrites, is observed at 20° to 103° and at a HNO_3 concn. of 5 to 20%. The amount of elementary S increases with the length of the treatment and with increase of temp. The presence of elementary S in the end-products of the reaction leads in several cases to perceptible errors in the determination of pyritic and organic S in coals.

C. D. KOPKIN

4217. **Nature of the fixed phase and of the carrier in gas - liquid partition chromatography of essential oils and aromatics.** Y.-R. Naves (L. Givaudan and Co., Ltd., Vernier, Geneva, Switzerland). *J. Soc. Cosmet. Chem.*, 1958, **9** (2), 101–103.—The influences of supporting and liquid phases, and of the operating conditions, on the analysis of essential oils by gas - liquid chromatography are discussed. Apparatus and conditions should be checked with reference samples before analysis is undertaken. Limitations for certain phthalates, polyoxyethylene glycols and their esters or ethers as the liquid phase are discussed, as also are silicones, the choice of carrier, and possible dehydrogenation of the alcohols.

G. HELMS

4218. **Determination of xanthate in viscose.** W. Fock (Centrallab. der Stora Kopparbergs Bergslags AB, Falun, Sweden). *Svensk Papp.-Tidn.*, 1957, **60** (24), 911–912.—Substances such as Na_2CS_3 and Na_2S, which interfere with the determination, are usually decomposed by the addition of acetic acid and chalk. Difficulties arise on account of the increasing temperature and the need to keep the chalk in even suspension. These have been overcome by using CO_2 (gas or solid), which decomposes interfering substances without having any action on viscose xanthate. The CO_2 also has a cooling action, enabling the temperature to be controlled. Viscose (2 g) is dissolved in water (200 ml) contained in a 500-ml three-necked flask, and CO_2 is then passed through the soln. for 15 to 20 min. The xanthate content of viscose is determined by titration with 0·1 *N* iodine.

E. DUX

4219. **Analysis of surface-active agents. III. Paper-electrophoretic separation.** Harutada Negoro and Setsuya Seno (Shinagawa Plant, Shinagawa-ku, Sankyo Co., Tokyo). *Ann. Rep. Takamine Lab.*, 1956, **8**, 119–122.—The paper-electrophoretic behaviour at 325 to 700 V and 1 mA per cm of cationic surfactants, benzalkonium (**I**) and benzethonium (**II**) hydrochlorides, was studied in acetate (pH 4·0), phosphate (7·0), barbitone (7·0) and borate (10·0) buffers. **I** and **II** are separated (colour reagent, 0·1% methyl orange) at pH 4·0 and 7·0 within 1 hr. Non-ionic surfactants of the polyoxyethylene alkylaryl ether type migrate towards the cathode at pH 10·0, the rate increasing with increase in the degree of polymerisation.

K. SAITO

4220. **Determination of starch in paper.** H. Feeser. *Stärke*, 1958, **10** (2), 39–41.—A critical survey of methods in general use is given. The main reason for variation in results obtained from different methods arises from the incomplete removal of starch from the paper fibre. This applies particularly to the TAPPI method, which uses saliva for the solubilisation of starch. However, the enzyme content of saliva varies from person to person. It was found that pancreatic amylase Diaferman KL proved an efficient agent for extraction of starch. After enzyme treatment, the starch was determined by the method of Hagedorn - Jensen. The accuracy of the whole procedure was $\pm$ 5% calculated on the starch content.

E. DUX

4221. **Spectrophotometric determination of phosphorus in polyethylene terephthalate.** G. Telep and R. Ehrlich (E. I. du Pont de Nemours & Co., Inc., Kinston, N.C., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1146–1148.—Semi-micro and micro-methods are described and are applicable to all difficultly oxidisable or slightly soluble materials. After oxidation with $HClO_4$ the complex formed with ammonium molybdate is reduced with hydrazine sulphate to form a heteropoly blue colour absorbing at 830 mμ. Arsenic and Ge interfere. With the semi-micro method, 5 μg of P per 50 ml can be accurately measured and with the micro-method 0·1 μg per 50 ml. A coeff. of variation of $\pm$7·4% was obtained on 15 samples.

K. A. PROCTOR

4222. **Paper chromatography in the analysis of polyesters.** I. Arendt and H.-J. Schenck (Chem.-Technol. Lab., Siemens-Schuckertwerke, Kabelwerk, Berlin-Siemensstadt). *Kunststoffe*, 1958, **48**, 111–113.—The polyester resin is saponified with alcoholic KOH, and the dicarboxylic acids are recovered by filtration of their potassium salts, dissolution in water and passage through a cation-exchange column; the glycols are recovered by evaporation of alcohol from the initial filtrate after neutralisation with ethanolic HCl. The acids are chromatographed in 2% alcoholic soln. on filter-paper, with a soln. of 300 g of phenol and 0·5 ml of formic acid in 100 ml of water for development, the individual members being made visible with 0·04% ethanolic bromocresol green soln. The undiluted glycols are chromatographed on paper, and developed in two directions with (*a*) $CHCl_3$ - ethanol (40:1), and (*b*) water-saturated ether, and made visible with 5% $AgNO_3$ soln. - 25% aq. NH_3 (9:1, by vol.).

J. L. PROSSER

4223. **Methods of testing plastics. Part 4. Analytical methods and viscosity in solution.** British Standards Institution (2, Park St., London, England). B.S. 2782:Part 4:1958, 27 pp.—Methods and apparatus are prescribed for the following determinations—matter soluble in acetone (in phenolic mouldings and in phenolic moulding material before and after moulding); analysis of the aq. extract of phenolic mouldings (ammonia and ammonium compounds, phenols, formaldehyde, sulphates, chlorides and pH); methanol-soluble matter and styrene in polystyrene; viscosity of soln. of poly(vinyl chloride) resins in *cyclo*hexanone and of soln. of polystyrene in toluole.

R. E. ESSERY

4224. **Determination of chlorine and fluorine in fluorocarbon plastics by fusion with potassium carbonate.** Rimpei Kijima and Hiroshi Ueno (Gov. Chem. Ind. Res. Inst., Nagoya, Hirate-machi, Kita-ku). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1958, **61** (2), 270–271.—The sample (0·5 g) is placed on K_2CO_3 (1 g) in a porcelain crucible, covered with K_2CO_3 (8 g) and heated to $\simeq 500°$ at a rate of $< 100°$ per hr. The cake is leached with water, filtered and diluted to 250 ml. An aliquot is titrated by the Volhard method. Another aliquot is passed through a column of Amberlite IR-122 into dil. NaOH soln. and a portion of the eluate is titrated with $Th(NO_3)_4$ by the usual method.

K. SAITO

4225. **Determination of the cholesterol and "*iso*-cholesterol" content of wool fat.** H. Janecke and G. Senft (Pharm. Inst., Univ. Frankfurt, Germany). *Pharm. Zentralh.*, 1957, **96** (8–9), 431–443.—The methods of estimating the cholesterol and "*iso*-cholesterol" content of wool fat and its preparations are reviewed. D. P. FELIX

4226. **Spectrophotometric determination of sterols in wool fat.** B. F. Putney and R. Calvo (Rutgers Univ. Coll. of Pharm., Newark, N.J., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (3), 205–210.—A modified procedure is given for the absorptiometric determination of cholesterol and "*iso*cholesterol" in wool fat, and for the determination of cholesteryl and "*iso*cholesteryl" esters in the unsaponifiable portion of wool fat, based on use of the Liebermann-Burchard reagent. The complexes of the esters absorb about 20% more light than those of the alcohols. The method involves the control of temp. at 30° and the determination of the extinctions of the various components at the times of max. colour development. The accuracy and precision are $\simeq \pm 2\%$. A. R. ROGERS

4227. **Infra-red quantitative analysis data.** *Anal. Chem.*, 1958, **30** (6), 1162; (7), 1303.—The following data have been published under the co-operative programme between *Analytical Chemistry* and the Coblentz Society of the U.S.A. **Determination of water, ethanol and benzene in ethyl bromide,** G. A. McCrory and R. T. Scheddel. **Analysis of 4-phenylphenol and 4:4'-biphenol mixtures,** L. R. Kiley. **Determination of water in phenylhydrazine,** L. R. Kiley and R. T. Scheddel. **Analysis of 4-bromodiphenyl and 4:4'-dibromodiphenyl mixtures,** L. R. Kiley.

Analysis of styrene-vinyl cyanide copolymers, R. T. Scheddel. **Analysis of aniline and 4:4'-methylenedianiline mixtures,** R. T. Scheddel. **Analysis of diphenylamine, diphenyl ether and azobenzene mixtures,** L. R. Kiley. **Determination of toluene in methyl*cyclo*hexane,** G. A. McCrory and R. T. Scheddel.

See also Abstracts—**4007**, Titration of oxalic acid. **4074**, Determination of H_2S and sulphides in products in the cellulose and viscose industries. **4110**, Determination of traces of iodine in organic materials. **4313**, Determination of citric acid. **4326**, Determination of acetylene in air. **4327**, Determination of carbonyl compounds in air.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

4228. **Spectrophotometric determination of chloride in sweat and serum with diphenylcarbazone.** J. L. Gerlach and R. G. Frazier (Dept. of Pediatrics, State Univ., Iowa City, U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1142–1146.—The sample is treated with ethanolic diphenylcarbazone soln. and $Hg(NO_3)_2$ soln., when a violet co-ordination compound is formed. The pH is adjusted to 3·2 with HNO_3 and the absorbance of the soln. at 520 mμ is determined spectrophotometrically. It is essential that purified diphenylcarbazone is used, and a purification procedure is described. The method is applicable to 0 to 240 μg of chloride per 100 ml with a precision of 1·6 μg per 100 ml and an accuracy of 2%. Bromide, cyanide, iodide and thiocyanate interfere, acetate, Cu^{2+} and Fe^{3+} interfere at concn. above 4 p.p.m., and oxalate and dichromate above 20 p.p.m. The method could be adapted to the determination of chloride in other media or, with modification, to the direct determination of Hg. S. M. MARSH

4229. **New method for the micro-determination of thallium in urine, blood and faeces.** N. V. Reĭs (Samarkand Med. Inst.). *Lab. Delo*, 1957, **3** (6), 12–16.—The method is based on the reaction of $TlCl_4^-$ with Brilliant green to form a salt-like compound that can be extracted with benzene or toluene to give a blue-green soln. with an absorption max. at 610 mμ. *Procedure*—To 1 ml of test soln. (containing 2 to 25 μg of Tl) in a wide test-tube add 4 ml of 5 *N* HCl and 2 ml of *N* $NaNO_2$. Shake and set aside for 5 min. Add 0·3 ml of a soln. of Brilliant green (1% in 25% ethanol), rapidly shake the contents of the tube and add 2·5 ml of toluene slowly from a micro-burette. Shake vigorously for 15 to 30 sec., separate the toluene layer and measure the extinction in a 5-mm cuvette in a photometer with filter S61, with a blank prepared with the reagents. For urine, add 2 ml of conc. HCl to 0·1 to 2 ml of sample and make up to 5 ml. Add 2 ml of *N* $NaNO_2$ and continue as described; centrifuging at 1500 to 2000 r.p.m. helps to separate the toluene layer. For blood, measure 0·1 (or 0·2) ml of blood into a test-tube containing 0·9 (or 0·8) ml of water. Add 4 ml of 5 *N* HCl, set aside on a boiling-water bath for 5 min., cool the soln. and proceed as for urine. For faeces, to a sample (300 to 400 mg) add water to make up to 2 g. Rub the mixture with a little powdered glass, add 8 ml of HCl (1:1), mix, and filter through a folded filter. Boil 5 ml of the filtrate on a water bath for 5 min. and then proceed as for urine.

E. HAYES

4230. **Screening method for glucose of blood serum utilising glucose oxidase and an indophenol indicator.** L. A. Dobrick (Bureau of Lab. of Milwaukee Health Dept., Wis., U.S.A.). *J. Biol. Chem.*, 1958, **231** (1), 403–409.—In the glucose-glucose oxidase reaction, 2:6-dichlorophenolindophenol can replace mol. O as the H acceptor, and there is a direct quant. linear relationship between the glucose oxidised and the indophenol reduced. A method for the approx. determination of glucose is described which is particularly applicable to the mass screening of many samples of blood serum for

glucose. It is unnecessary to remove protein, and the glucose concentration of serum or plasma can be directly classified, with an error of 10 mg per 100 ml, as being above or below any predetermined screening level. J. N. ASHLEY

4231. **Determination of glucose and laevulose [fructose] in body fluids.** J. Ek and E. Hultman (Clinical Lab., St. Erik's Hospital, Stockholm). *Nature*, 1958, **181**, 780–781.—Two methods are described, both of which are based on the measurement of the colour produced when monosaccharides are condensed with certain aromatic amines in glacial acetic acid. (*i*) *p*-Aminobenzoic acid is used for the condensation, and reacts with aldoses, but only slightly with ketoses. (*ii*) *m*-Aminophenol condenses with both aldoses and ketoses. The methods are simple to apply, but reagent purity is critical. G. S. ROBERTS

4232. **Estimation of tartronate in tissues.** L. G. Wesson (Dept. of Biology, M.I.T., Cambridge, Mass., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1080–1083.—A method for the determination of tartronate (hydroxymalonate) in plant and animal tissues is described. The method is based on the decarboxylation of tartronic acid by dil. H_2SO_4 and the spectrophotometric determination of the glycollic acid formed after treatment with Eegriwe's reagent (20 mg of 2:7-dihydroxynaphthalene in 100 ml of H_2SO_4). Details are also given of the method for extracting tartronate from the sample. An evaluation of the procedure indicated that no decarboxylation occurs during dialysis of the sample or purification of the dialysate, and that identification and estimation of tartronate in tissues is possible. S. M. MARSH

4233. **Determination of the ascorbic acid content of blood by Tillmans method.** B. G. Belen'kiĭ. *Lab. Delo*, 1957, **3** (6), 7–11.—In the determination of ascorbic acid in blood by titration with 2:6-dichlorophenolindophenol, trichloroacetic acid is unsuitable as a protein precipitant. It is recommended that metaphosphoric acid at pH 1·85 to 2·0 should be used. E. HAYES

4234. **Simple volumetric method for the determination of uric acid in urine.** L. A. Maĭ (Republican Blood Transfusion Station, Riga, USSR). *Lab. Delo*, 1957, **3** (5), 41–43.—Uric acid reduces tungstophosphate in alkaline soln. and the dark-blue complex formed is titrated against $K_3Fe(CN)_6$ until the soln. is colourless. The $K_3Fe(CN)_6$ soln. is standardised against Li urate. Of the reducing substances that occur in urine, only L-ascorbic acid interferes. When necessary this is determined by titration with 2:6-dichlorophenolindophenol and a correction is applied. E. HAYES

4235. **Quantitative determination of xanthines and uric acids in plasma.** F. Bergmann, S. Dikstein and M. Chaimovitz (Hebrew Univ.-Hadassah Med. School, Jerusalem). *J. Biol. Chem.*, 1958, **230** (1), 193–201.—Deproteinisation of plasma with $HgCl_2$ makes possible the quant. analysis by paper chromatography of substituted xanthines and uric acids that cannot be determined by enzymatic methods. After treatment with $HgCl_2$ and removal of excess of Hg with H_2S, the filtered soln. is boiled to remove H_2S, adjusted to pH 1 and passed through a column of Dowex 50-X4 or -X16 (H^+) which is then washed with 0·5 *N* HCl. The eluate containing the uric acids is evaporated to dryness and extracted with Li_2CO_3 soln. The extract is subjected to two-dimensional paper chromatography with 95% ethanol - pyridine - water (7:2:1, by vol.) followed by 95% ethanol - water - acetic acid (17:2:1, by vol.). The paper is cut into strips in the direction of the second solvent, the strips are extracted with 0·05 *M* borax and the extinction is determined at the wavelengths characteristic of the individual components. The xanthines are eluted from the resin with 10% aq. NH_3 (6 × 20 ml). The eluate is evaporated and extracted with Li_2CO_3 soln. It is then chromatographed in the same way, but with 95% ethanol - water - acetic acid only. Blanks are carried out on plasma alone and the extinctions subtracted from the extinctions of the corresponding strips. The recovery of theophylline (5·7 μg per ml) and 1:3-dimethyluric acid (9 μg per ml) was 95% and 90%, respectively. N. E.

4236. **Quantitative determination of xanthines and uric acids in urine.** S. Dikstein, F. Bergmann and M. Chaimovitz (Dept. of Pharmacol., Hebrew Univ.-Hadassah Med. Sch., Jerusalem, Israel). *J. Biol. Chem.*, 1958, **230** (1), 203–211.—The xanthines and uric acids are adsorbed on a cation-exchange resin, such as Dowex 50, which has been pretreated with Hg^{2+}. They are then eluted, together with Hg^{2+}, by 3 *N* HCl; the Hg is removed as HgS, and the resulting soln. of the purines is passed down a column of Dowex 50. The purines are then determined spectrophotometrically after separation by paper chromatography, as described for their determination in plasma (*cf. Anal. Abstr.*, 1958, **5**, 4235). J. N. ASHLEY

4237. **Some additions to the method or the determination of riboflavine in urine.** A. P. Rŷzhova. *Lab. Delo*, 1957, **3** (5), 39–41.—The method of Malennikova and Gvozdeva [*Voprosy Pitaniya*, 1956, (2), 25] for the determination of riboflavine in urine gives satisfactory results, but proteins must first be pptd. To remove proteins, $(NH_4)_2SO_4$ (8 g) is ground with a sample of urine (10 ml) and, after 15 to 20 min., the pptd. protein and undissolved $(NH_4)_2SO_4$ are filtered off. A sample of protein-free urine, freed from riboflavine by heating with alkali, is titrated with riboflavine soln. in u.v. light until the intensity of fluorescence is the same as that of a test sample. The extraneous blue colour of the urine is eliminated by means of a filter cutting off light of wavelength < 550 mμ. Acetic and sulphosalicylic acids are unsatisfactory as protein precipitants. E. HAYES

4238. **Determination of small quantities of bilirubin in urine.** M. P. Bolotov. *Lab. Delo*, 1958, **4** (1), 21–24.—To 50 ml of fresh unfiltered urine add 5 drops of acetic acid and 20 drops of a soln. of Pb acetate (10 g, 3 g of acetic acid and 100 ml of H_2O). Filter and wash the ppt. with H_2O. Unfold the filter on dry filter-paper and cut it into two or three parts; transfer the pieces to a white paper and moisten with 4 or 5 drops of chloramine-B reagent (chloramine B 1·0 g, NaCl 3·0 g, conc. HCl 5 ml, H_2O 100 ml) or dichromate reagent ($K_2Cr_2O_7$ 0·05 g, $FeCl_3$ 2·0 g, H_2SO_4 5·0 g, cryst. Na_2SO_4 20·0 g, H_2O 100 ml). A blue spot is produced by $\pm$ 0·005 mg of bilirubin. For the rapid detection of bilirubin, drop 10 drops of urine on to a plate (2 cm × 2 cm × 5 mm), made by mixing gypsum and talc (10:1) with water and drying; if the urine contains $\pm$ 0·07 mg % of bilirubin, the spot on the plate will turn blue when it is moistened with the chloramine-B reagent. E. HAYES

4239. **Quantitative determination of methanol in forensic materials.** I. Odler (Inst. Forensic Med., Komenský Univ., Bratislava, Czechoslovakia). *Soudní Lékařství*, 1957, **2** (4), 49–54.—*Procedure*—To the ground material (100 g) add tartaric acid and distil off 50 ml. To 10 ml of the distillate add H_2SO_4 (25%) (5 ml), ethanol (0·5 ml) and $KMnO_4$ (5%) (2 ml), and after 5 min. a satd. soln. of oxalic acid (2 ml). Add 5 ml of reagent (dissolve 0·1 g of fuchsine in 500 ml of water, add 6 g of Na_2SO_3 and 10 of 25% HCl and make up to 1 litre), set aside for 1 hr. and measure the colour with the use of a S57 filter (Pulfrich photometer). J. ZÝKA

4240. **Determination of epinephrine [adrenaline] and related compounds on paper chromatograms.** G. L. Ellman (Biochem. Res. Lab., Dow Chem. Co., Midland, Michigan). *Nature*, 1958, **181**, 768–769.—These catechols are separated on paper with *tert.*-butyl alcohol - formic acid - water (40:1:10). The dried paper strips are treated with aq. ethylenediamine [5%, containing 0·1% of $K_3Fe(CN)_6$ or iodine to a concn. of 0·01 *N*] by spraying, or by a dipping procedure. The spots produced are fluorescent and can be determined spectrophotometrically. G. S. ROBERTS

4241. **Method for the estimation of adrenaline and noradrenaline in urine.** T. B. B. Crawford and W. Law (Dept. of Pharmacol., Univ. of Edinburgh). *J. Pharm. Pharmacol.*, 1958, **10** (3), 179–188.—To determine adrenaline (**I**) and noradrenaline (**II**) in urine, adsorb 24-hr. specimens of rat or human urine, containing ascorbic acid as antioxidant, on Amberlite IRC-50 cation-exchange resin at pH 7 and elute with dil. H_2SO_4. If the concn. of **I** + **II** in the eluate is < 0·5 p.p.m., add ethanol - acetone (1:1), allow the mixture to stand overnight at 5°, filter and evaporate. Oxidise with MnO_2 at pH 6·5, make alkaline and measure the fluorescence, using as blank a similarly treated soln. containing ascorbic acid (*cf.* Lund, *Brit. Abstr. C*, 1950, 409; 1951, 223). The recovery is ≃ 80%. To determine **I** and **II** separately, transfer the evaporated desalted eluate from the resin to Whatman No. 1 paper and develop with phenol - 0·1 *N* HCl (20:3, by wt.) in an atmosphere of N (*cf.* Crawford and Outschoorn, *Brit. J. Pharmacol.*, 1951, **6**, 8). The recovery of each component is ≃ 50%. The analytical results may be corrected by means of control experiments performed with each series of analyses. A. R. ROGERS

4242. **Determination and excretion of polyhydroxy (catecholic) phenolic acids in urine.** S. L. Tompsett (Biochem. Lab., Northern General Hospital, Edinburgh). *J. Pharm. Pharmacol.*, 1958, **10** (3), 157–161.—The Mitchell reaction (*cf. Analyst*, 1923, **48**, 2) is used to determine pyrogallol, gallic acid, 3:4-dihydroxybenzoic acid and caffeic acid in urine to within ± 10%. Catechol is not recovered, and ferulic acid, vanillic acid and syringic acid do not interfere. Gallic acid, 3:4-dihydroxybenzoic acid and caffeic acid may be separated by descending chromatography on Whatman No. 1 paper with *n*-butanol - acetic acid - H_2O (4:1:5) as solvent; the R_F values are ≃ 0·6, 0·8 and 0·9, respectively. *Procedure*—Heat the urine sample (10 ml) with 10 *N* HCl (1 ml) on a boiling-water bath for 1 hr., then cool. Extract with ether (3 × 40 ml) and allow the ether to evaporate at room temp. Pyrogallol may be quant. removed from the residue by evaporating twice with ethanol (80 ml) under reduced pressure. Dissolve the residue in H_2O (0·5 ml), and add a soln. of $FeSO_4.7H_2O$ (0·5 mg) and Na K tartrate (2·5 mg) in H_2O (0·5 ml), 10% ammonium acetate soln. (10 ml) and 2 *N* aq. NH_3 (1 ml) to give a pH of 7·8. After 20 min., measure the extinction at 560 mμ against a reagent blank. A. R. ROGERS

4243. **Further studies on the mechanism of transamidinase action: transamidination in *Streptomyces griseus*. [Determination of hydroxyguanidine.]** J. B. Walker (Dept. of Biochem., Baylor Univ. Coll. of Med., Houston, Texas, U.S.A.). *J. Biol. Chem.*, 1958, **231** (1), 1–9.—The determination is similar to that used by Fearon and Bell (*Anal. Abstr.*, 1955, **2**, 1362) for the assay of canavanine. *Procedure*—Add an aliquot of the unknown soln., with sufficient water to make 2·0 ml, to a test-tube (13 mm × 100 mm); then add *M* K_2HPO_4 buffer (pH 7·0) (2 ml) and 1% aq. sodium pentacyanoamminoferrate (0·3 ml) (prepared from sodium nitroprusside and aq. NH_3); mix thoroughly and measure colorimetrically the extinction at 480 mμ. The amount of hydroxyguanidine is ascertained from a standard graph. When hydroxylamine is present, its inhibitory effect is minimised by addition of acetone to form acetoxime. J. N. ASHLEY

4244. **The biosynthesis of trehalose phosphate. [Determination of uridine 5′-pyrophosphate].** E. Cabib and L. F. Leloir (Inst. de Investigaciones Bioquím., Obligado 2490, Buenos Aires, Argentina). *J. Biol. Chem.*, 1958, **231** (1), 259–275.—Uridine 5′-phosphate and trehalose phosphate are formed by an enzymic-catalysed reaction between uridine diphosphate glucose and glucose 6-phosphate. A method for the determination of uridine 5′-phosphate is based on the transfer of phosphate from phosphopyruvate to uridine 5′-phosphate by pyruvate kinase. The pyruvate liberated is determined colorimetrically at 520 mμ, after addition of dinitrophenylhydrazine, according to the method of Friedemann and Haugen (*Brit. Abstr. AIII*, 1943, 616). J. N. ASHLEY

4245. **Turbidimetric determination of lysozyme in animal gastric juice.** M. E. Goldberg and G. V. Rossi (Philadelphia Coll. of Pharmacy and Sci., Pa.). *Amer. J. Pharm.*, 1958, **130** (3), 78–81.—Lysozyme (**I**) lyses, and hence reduces the turbidity of, suspensions of *Micrococcus lysodeikticus* (**II**). The content of **I** in gastric juice may be determined by comparing the reduction in optical density of suspensions of **II** caused by the sample with that due to standards prepared from cryst. egg-white lysozyme. A blank determination is required, since gastric juice also contributes to the turbidity. The accuracy of the method is ± 5%. A. G. COOPER

4246. **Bis-(*p*-dimethylaminophenyl)amine as a reagent for the characterisation of fatty acids.** Sukumar Das and S. C. Niyogy (Univ. Coll. Sci. Technol., Calcutta). *Ann. Biochem., Calcutta*, 1956, **16**, 5–8.—Dissolve 0·5 g of the disubstituted amine in 25 ml of dry ether and filter the soln. Dissolve an equiv. amount of fatty acid in dry ether. Mix the two soln. and heat under reflux on a water bath for 1 hr. As the reaction proceeds, a ppt. forms. Evaporate off the solvent and recrystallise the ppt. from ethanol. Details are given for the preparation of the reagent. CHEM. ABSTR.

4247. **Dyeing method for quantitative determination of lipids and lipoproteins directly on filter-paper [electropherograms].** K. F. Talluto, R. R. Benerito and W. S. Singleton (Southern Utilization Research and Development Div., U.S. Dept. Agric., New Orleans, La.). *Anal. Chem.*, 1958, **30** (6), 1059–1062.—After a review of previous work on the development of lipid-dyeing techniques, a new procedure for the estimation of lipids on paper strips is described. The method was particularly designed for measuring accurately and rapidly changes in serum-lipid fractions after the administration of intravenous fat emulsions. The dye bath used is a 50% aq. soln. of glycerol diacetate saturated with Oil Red O. Di- and tri-glycerides do not wash off the paper strips during dyeing as often occurs with alcoholic dye baths. A minimum dyeing period of 16 hr. at 25° is necessary to ensure linear relationship between the amount of dye absorbed and the quantity of lipid on the strip. After drying, the dyed strips are sprayed with 1-bromonaphthalene soln. to minimise light scattering and examined by transmission densitometry, which measures the dye uptake directly. The validity of the method was tested on human serum and canine serum. S. M. MARSH

4248. **Estimation of serum phospholipid and total phosphorus using chloric acid.** J. F. Goodwin, R. Thibert, D. McCann and A. J. Boyle (Wayne State Univ., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1097–1099.—The serum is digested with $HClO_3$ and the resulting soln. is treated with sodium molybdate and hydrazine sulphate, when a stable blue colour is formed by reduction of the molybdophosphoric acid complex. The absorbance of the soln. is then measured at 830 mμ or 655 mμ. The method is suitable for routine analysis since individual attention during digestion is unnecessary. Advantages are high sensitivity and colour stability. As little as 5 μg of P may be determined at 830 mμ, and the procedure can be scaled down for even smaller amounts. S. M. MARSH

4249. **Identification of phosphatides by paper chromatography.** U. Beiss and O. Armbruster (Bundesforschanstalt f. Viruskrankheiten der Tiere, Tübingen, Germany). *Z. Naturf.*, 1958, **13b** (2), 79–84.—The chromatographic runs are carried out at constant temp. and in the dark. S. & S. papers 2043b Mgl and 2045b Gl were found suitable but silicone-impregnated paper or acetylated paper did not give satisfactory results. Five different solvent mixtures were investigated with satisfactory results and the following pair is recommended for a two-dimensional run—for the first direction to be run at right angles to the direction of the paper fibre a mixture of tetrahydrofuran - di*iso*butyl ketone - water (45:5:6, by vol.), and for the second direction a mixture of di*iso*butyl ketone - *iso*butyl methyl ketone - ethyl methyl ketone - chloroform - formic acid - water (30:26:20:110:30:3, by vol.). With this arrangement a paper square of 14 cm × 14 cm is sufficient and only 4 hr. is required for the completion of the two-dimensional run. The phosphatides are identified by applying three reactions in succession to the paper—(*i*) ninhydrin (for NH_2 groups, serine, ethanolamine); (*ii*) dipicrylamine (for choline); (*iii*) rhodamine B (for higher fatty acids and aldehydes). A list of R_F values of pure substances is presented. E. KAWERAU

4250. **Purity test for amino-acid preparations.** E. Schulek and Z. L. Szabó (Inst. for Inorg. and Anal. Chem., L. Eötvös Univ., Budapest). *Z. anal. Chem.*, 1957, **157** (6), 405–411.—The purity of amino-acid prep. can be tested by paper chromatography. After development of the chromatogram, the nitrogen content of the spots of the amino acids is determined. An approx. estimation of contaminating amino acids is obtained from a knowledge of the "upper paper-chromatographic limit" (the amount that no longer gives a well-defined spot) of the major constituent, and the lowest amount of the impurity that can be identified. Amino-acid prep. that show no trace of impurity at this "upper limit" are described as "paper-chromatographically pure". J. H. WATON

4251. **Chromatography of amino acids on sulphonated polystyrene resins. An improved system.** S. Moore, D. H. Spackman and W. H. Stein (Rockefeller Inst. for Med. Res., New York, N.Y.). *Anal. Chem.*, 1958, **30** (7), 1185–1190.—Improved procedures for the chromatographic determination of amino acids, on columns of finely pulverised 8% cross-linked sulphonated polystyrene resins, are described. The smaller particle size enables higher flow rates to be used and appropriate choice of eluents simplifies operations. Analyses of synthetic mixtures gave recoveries of 100 $\pm$ 3% for $\simeq$ 20 amino acids. G. P. COOK

4252. **Amino-acid analysis by reactor-gas chromatography.** A. Zlatkis and J. F. Oró (Univ. of Houston, Tex.). *Anal. Chem.*, 1958, **30** (6), 1156.—A special reactor-gas chromatography unit is used. The amino-acid soln. is injected into a system of continuously flowing hydrogen where it is first treated in a micro-reactor containing 30% ninhydrin on diatomaceous earth at 130°. Instant oxidation to volatile aldehydes occurs and these are passed to a chromatographic column containing silicone oil on Celite, where separation is achieved. As each aldehyde leaves the column it is cracked in a second micro-reactor containing a nickel-kieselguhr catalyst at 425°, to give methane and water. Water is absorbed in a Drierite column and the amount of methane is measured in a thermal-conductivity cell. Mixtures containing alanine, α-amino-*n*-butyric acid, valine, *nor*valine, leucine *iso*leucine and *nor*leucine have been analysed, and quant. results so far obtained indicate that 1 μg of an amino acid can be detected. The procedure overcomes difficulties caused by the presence of water in the soln. to be analysed, sensitivity is increased and calibration is eliminated. The method is limited to amino acids that can be oxidised to volatile aldehydes, excluding glycine, since the formaldehyde formed from it polymerises. S. M. MARSH

4253. **Automatic equipment for determination of amino acids separated on columns of ion-exchange resins.** D. H. Simmonds (Wool Textile Res. Lab., C.S.I.R.Θ., Melbourne, Australia). *Anal. Chem.*, 1958, **30** (6), 1043–1049.—A detailed description with diagrams and illustrations is given of equipment which has been developed for the automatic colorimetric determination of amino acids separated chromatographically. All manipulations, with the exception of loading the columns and changing buffers, are carried out automatically and analytical variations have been reduced by a factor of 3 over the normal method. The equipment is cheaper than that described by Spackman *et al.* (*Federation*

Proc., 1956, **15**, 358) and results are easier to interpret, being recorded as a single point graph, but disadvantages are that the maximum speed of operation is just under four 2-ml fractions per hour and that proline cannot be estimated unless the filter of the spectrophotometer is changed manually at the correct time. Typical recorder traces are shown for a protein hydrolysate and a synthetic mixture of amino acids, and a table is given for the conversion of transmittance figures into absorbance units. The equipment may be applied to the estimation of other groups of materials separated by chromatography, provided that there is a common colorimetric, absorptiometric or turbidimetric analytical procedure. S. M. MARSH

4254. **Ion-exchange resins in single columns and coupled columns. Separation of some amino acids and of riboflavine phosphates.** P. Cerletti, G. Montesi and N. Siliprandi (Ist. Chim. Biol., Univ. Rome). *Arch. Sci. Biol., Bologna*, 1957, **41**, 554–558.—The coupled columns were three, of diameters 10, 8·9 and 7 mm and lengths 54, 38·7 and 30·5 mm, respectively. The single column used for comparison was 8·9 mm in diameter and 120 mm long and contained the same amount of resin as in the coupled columns. The carboxylic resin was Amberlite IRC-50. There was no substantial difference in the results obtained by the two methods, but the peaks with coupled columns were sharper and this method is preferred. NUTR. ABSTR. & REV.

4255. **Quantitative determination of hydroxyproline by paper chromatography.** H. R. Roberts and M. G. Kolor (Res. Lab. Div., Nat. Dairy Products Coop., Oakdale, L.I., N.Y., U.S.A.). *Nature*, 1958, **181**, 837.—The maximum colour density method for the quant. analysis of amino acids (*cf. Anal. Chem.*, 1957, **29**, 1800) has been improved for hydroxyproline by the use of a reagent comprising ninhydrin, isatin and triethylamine in *n*-butanol instead of isatin only. The standard deviation was reduced from 3·4% to 0·9%. S. BAAR

4256. **Colorimetric method for the estimation of tyrosine.** J. H. Ottaway (Dept. of Biochem., Univ. Coll., London). *Biochem. J.*, 1958, **68** (2), 239–244.—A simple and reliable method for the determination of 10 to 250 μg of tyrosine in 2 to 4 ml of soln. is described. *Procedure*—To the soln. (2 ml) add the reagent (0·1 ml of 0·3% 1-nitroso-2-naphthol in acetone); mix the contents and heat the tube in a water bath at 60° for 5 min. Remove the tube and carefully add conc. HNO_3 (4 drops) so that the drops fall through the soln. and do not touch the walls of the tube. Replace the tube in the bath taking care not to disturb the layer of acid. After heating for 1 min. mix the contents by swirling, cool in air for $\simeq$ 5 min., and add a stabilising reagent (aq. NaCl - acetone - $FeCl_3$) (6 ml); the composition and vol. of the reagent can be altered, but the final soln. should contain 0·12 *M* NaCl and 25% of acetone. Determine the colour intensity within 10 to 45 min. with an OB2 filter and the EEL colorimeter. The amount of tyrosine is then ascertained from a standard graph. The method is easily applicable to the determination of tyrosine in protein hydrolysates and in urine if precautions are taken against interference by tryptophan. If the urine is diluted 10 to 20-fold and internal standards are also used, the estimation is performed without difficulty. J. N. ASHLEY

4257. **Determination of cysteine with ferricyanide by amperometric titration with two polarised electrodes.** H. G. Waddill and G. Gorin (Dept. of Chem., Oklahoma State Univ., Stillwater, U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1069–1071.—Amounts of cysteine between 1 and $1{\cdot}5 \times 10^{-3}$ millimole can be determined with a precision within 1% by direct titration with $K_3Fe(CN)_6$ at pH 7 with two platinum electrodes. The end-point is reached when a direct current due to excess of reagent is indicated. Samples must be protected from oxidation conditions. As other amino acids do not interfere, the method can be applied to amino-acid mixtures. K. A. PROCTOR

4258. **Determination of cysteic acid in keratin by high-tension paper electrophoresis.** H. Zuber, K. Ziegler and H. Zahn (Chem. Inst., Univ. Heidelberg). *Z. Naturf.*, 1957, **12b** (8–9), 531–534.—The best separation of cysteic acid from glutamic and aspartic acids is obtained when the pH of the pyridine - acetic acid buffer is 3·5. High-tension electrophoresis is carried out on S. & S. 2043a paper (115 cm × 14 cm) and the run is made with an overall current of 5000 V, 15 mA and a coolant at − 10°. Under these conditions, cysteic acid migrates 7 to 12 cm towards the anode in 90 min. The ninhydrin - cysteic acid complex on the paper is converted into its copper derivative, which is eluted and determined spectrophotometrically at 540 mμ. Quant. results for wools that have undergone different processes are presented. E. KAWERAU

4259. **Modification of the diacetyl method for determining creatine and phosphocreatine.** W. Drabikowski (Zakl. Biochem. Inst. Biol. Dóswiad im M. Nenchiego). *Acta Biochim. Polon.*, 1957, **4**, 41–48.—The modification consisted in the use of 8-hydroxyquinoline instead of 1-naphthol. The reagent was added as a soln. in acetic acid or as an aq. soln. of the sulphate. It is more stable than 1-naphthol and there is no side reaction with trichloroacetic acid. From 10 to 40 μg of creatine in a sample can be determined. NUTR. ABSTR. & REV.

4260. **A tracer method for the determination of microgram quantities of protein.** A. M. Shefner, R. Ehrlich and H. C. Ehrmantraut (Biol. and Bact. Res., Armour Res. Foundation, Illinois Inst. of Technol., Chicago). *Intern. J. Appl. Radiation Isotopes*, 1957, **2** (1), 91–92.—The protein is pptd. by the addition of K_2WO_4 labelled with ^{185}W in KOH soln.; sufficient HCl is first added to the protein soln. to neutralise the KOH and to reduce the pH value below the isoelectric point of the protein. After being filtered off, the ppt. is dried and counted, and the weight of protein is deduced by reference to a calibration curve. The curves are linear over the range 1 to 10 μg for gelatin and bovine albumin. G. J. HUNTER

4261. **Chromatography of sterols, steroids and related compounds.** [**I, II.**] R. Neher (Ciba A.-G., Basel, Switzerland). *J. Chromatography*, 1958, **1** (2), 122–165; (3), 205–258 (in German).—A comprehensive review, with specific reference to paper chromatography. (389 references.) A. R. ROGERS

4262. **Determination of free cholesterol in serum without extraction.** J. F. Torres (Univ. Nac. del Sud, Argentina). *Rev. Asoc. Bioquim. Argentina*,

1957, **22**, 336–341.—*Cobalt reagent*—Dissolve 85·5 mg of $CoCl_2.5H_2O$ in 2 ml of double-distilled water, add 5 ml of glacial acetic acid and dilute to 100 ml with conc. H_2SO_4. *Procedure*—Mix 0·1 ml of serum with 0·3 ml of glacial acetic acid, 0·1 ml of water and 1 ml of digitonin soln. (1% ethanolic, w/v) and centrifuge for 5 min. (2500 rev.). Decant the supernatant liquid and wash the ppt. with water then acetone, and finally dissolve it in 6 ml of hot glacial acetic acid. Cool, add 4 ml of the cobalt reagent and measure the extinction at 500 mμ. The recovery was 87 to 100%. A Crudo - Caamaño instrument and No. 50 filter were used.
G. H. FOXLEY

4263. **Reversed-phase partition chromatography of some C_{27} steroids. Bile acids and steroids.** H. Danielsson (Lund Univ., Sweden). *Biochim. Biophys. Acta*, 1958, **27** (2), 401–405.—Aqueous *iso*propyl alcohol (50 to 55%) is used as mobile phase and 20% $CHCl_3$ in heptane as stationary phase on columns of Hyflo Supercel prepared by the method described. Elution patterns with this and other phase systems, suitable for the purification of different neutral hydroxy- and keto-steroids, and for biological work with such substances, are given.
W. H. C. SHAW

4264. **Chromatographic separation of oestriol, oestrone and oestradiol-17β.** Tokuichiro Seki (Dept. of Genetics, Faculty of Med., Osaka Univ., Japan). *Nature*, 1958, **181**, 768.—A carboxylic acid type, cation-exchange resin (Amberlite IRC-50) is partially esterified with a mixture of ethanol and dil. HCl, and used in the columnar chromatographic separation of oestrogens.
G. S. ROBERTS

4265. **Qualitative, quantitative and preparative chromatography of steroids on fully acetylated paper.** F. J. Ritter and J. Hartel (Central Lab., T.N.O., Delft, Holland). *Nature*, 1958, **181**, 765–766.—Fully acetylated paper has been found to have advantages over impregnated and partially acetylated paper. The method of Zijp (*Anal. Abstr.*, 1955, **2**, 3526) with a two-phase mixture of benzene, methanol and water (4:4:1) gives a good separation of steroids of widely differing polarity. The method has been applied to male sex hormones, progesterone, corticosteroids and their acetates, bile acids, and cholesterol and its oxidation products. The ascending technique was used in all separations.
G. S. ROBERTS

4266. **The determination of formaldehydogenic steroids by diffusion and its physiopathological applications.** P. Desgrez, J. Haas and S. H. Weinmann. *Ann. Biol. Clin., Paris*, 1957, **15**, 289–304.—A 24-hr. urine is collected, preserved with $Hg(SCN)_2$ (0·01 g per litre), and stored in the refrigerator. An aliquot (10 ml) is adjusted to pH 5·2 with 5 ml of acetate buffer. Steroids are hydrolysed by the addition of 5 parts per 100 parts of snail extract and incubated at 37° for 24 hr. Steroids are extracted with $CHCl_3$ in a special apparatus (Henry and Thevenet, *Bull. Soc. Chim. Biol.*, 1952, **34**, 886), and the $CHCl_3$ layer is washed with 0·1 *N* NaOH and H_2O and dried below 60° *in vacuo*. The residue is diluted with abs. ethanol so that 1 ml ≡ 5 ml of urine. Aliquots of urine extracts and standards are evaporated to dryness and dissolved in 0·1 ml of triethyl phosphate. Bromothymol blue (2 drops) and periodic acid (1 ml) (0·02 *M* in 0·6 *M* H_2SO_4) are added, followed by sufficient K_2AsO_3 (20%) to change the colour of the indicator to blue. The soln. is finally diluted to 2·5 ml with H_2O. An aliquot is placed in the outer chamber of a Conway cell. The central chamber contains 2 ml of colour reagent (150 mg of chromotropic acid and 35 ml of conc. H_2SO_4, diluted to 50 ml with H_2O). The unit is sealed and incubated at 37° for 18 to 20 hr. The contents of the centre chamber are transferred to a test-tube, heated in a water bath for 30 min., and read at 520 mμ.
CHEM. ABSTR.

4267. **Micro-method for determining total 17-hydroxysteroids of plasma.** A. Brancaccio, B. D'Alessandro and R. De Luca (Univ. Naples). *Folia Endocrin., Pisa*, 1957, **10**, 279–285.—The method of Reddy *et al.* (*Anal. Abstr.*, 1956, **3**, 2542) was modified as follows. Put 5 ml of plasma (from heparinised blood) into a centrifuge tube, add 10% $ZnSO_4$ soln. (2·5 ml) and 0·5 *N* NaOH (2·5 ml), shake, centrifuge for 30 min., remove the supernatant liquid, acidify to pH 1 with 50% H_2SO_4 soln., add 2 g of Na_2SO_4 and 5 ml of butanol, shake vigorously for 5 min., then centrifuge for 5 min. Separate the butanol phase, add 0·2 g of Na_2CO_3, and shake for 5 min., set aside for 5 min., then centrifuge, and dry a 4-ml aliquot at 80° to 85° (carry out this drying operation also for 4 ml of butanol and for 4 ml of a soln. containing 250 μg of standard 17-hydroxysteroid per 100 ml of butanol). Prepare a soln. comprising 4 parts of 62% H_2SO_4 and 1 part of ethanol, add 2·5 ml to each of the three dried butanol soln., warm at 60° for 20 min., read the extinction at 410 mμ (*a*, *b* and *c*, respectively, for blank, standard and sample), add 0·1 ml of reagent (175 mg of phenylhydrazine hydrochloride in 10 ml of 62% H_2SO_4) to each tube, warm again at 60° for 20 min. and read again at 410 mμ (*A*, *B* and *C*, respectively). Subtract *a*, *b* and *c*, respectively, from *A*, *B* and *C* (to give *A'*, *B'* and *C'*). Then μg of hormone per 100 ml of plasma = $[(C' - A' \times 10)/(B' - A')] \times 25$.
CHEM. ABSTR.

4268. **Semi-micro method for routine determination of urinary 17-hydroxycorticosteroids.** F. G. Sulman (Hebrew Univ., Jerusalem). *Acta Endocr., Copenhagen*, 1956, **22**, 107–114.—Place 2-ml samples of the 24-hr. urine samples in small penicillin bottles and set up (*a*) three bottles containing 2 ml of water as blanks and (*b*) three bottles containing 2 ml of water and 10, 20 or 30 μg of cortisone as standards. Add two drops of 56% H_2SO_4 to give a pH of 2 and 2 ml of *n*-butanol to each bottle and place uncovered in a water bath at 60° for 10 min. Remove, stopper and shake for 30 sec. Centrifuge and remove quant. the lower aq. layer. Now add 0·15 g of Na_2CO_3 and shake for 30 sec. Remove the butanol soln. quant. and distribute it each equally into two colorimetric tubes. To one tube add 5 ml of 56% H_2SO_4 (blank) and to the second add 5 ml of phenylhydrazine reagent (65 mg of phenylhydrazine hydrochloride in 56% H_2SO_4). Shake well, incubate for 40 min. in a water bath at 60°, remove, cool, and carry out colorimetry at 410 to 440 mμ with a blue filter. The 17-hydroxycorticosteroid value is obtained from a calibrated standard curve.
G. F. SOMERS

4269. **Separation, detection and estimation of $C_{(21)}$ 17:20-dihydroxy-20-methylsteroids.** R. I. Cox (Dept. of Vet. Physiology, Univ. of Sydney, Australia). *Nature*, 1958, **181**, 638–639.—All the known members of this group of steroids are detectable on paper chromatograms by heating with

H_3PO_4 (70%) and examining in daylight or u.v. light. Separation can be achieved on a descending paper chromatogram with benzene and formamide mixtures. The individual steroids can be determined, without extraction from the paper, by the amount of acetaldehyde formed by oxidation of the $C_{(17)}$ side-chain. G. S. ROBERTS

4270. **Paper chromatography of weakly polar steroids. Additions to the method of Neher and Wettstein.** F. J. Loomeijer and G. M. Luinge (Dept. of Physiol. Chem., Univ., Groningen, Holland). *J. Chromatography*, 1958, **1** (2), 179–181.—The method of Neher and Wettstein (*cf. Brit. Abstr. C*, 1952, **303**) consists in immersing the paper in 10% 2-phenoxyethanol (**I**) in ether, removing and blotting, applying the steroids in ether soln., exposing the paper to the air for a given time ("time of application") at a given temperature ("temp. of application"), then at once transferring the paper to the chromatographic tank and developing for 135 min. by the ascending technique with heptane satd. with **I**. The amount of **I** in the paper determines the reproducibility of the R_F values, the optimum being about 15% of **I** at the end of the time of application. Increasing time and temp. of application tend to increase R_F values, but the temp. of the actual chromatography has no influence. Steroids of very low polarity are best separated on Whatman paper No. 7 and 4, those of higher polarity on No. 1 or 3, those of still higher polarity by using 2-methoxyethanol instead of **I** in the solvent system. Weakly polar steroids are separated by a short time of application and low temp. ($<$ 15 min. and 0°), those of higher polarity by a time of 15 to 30 min. and temp. $>$ 19°. For reproducibility, these two factors, together with the amount of **I** in the paper, must be strictly controlled. R. E. ESSERY

4271. **Simple micro-titrimetric constant-pH method for accurate enzyme analysis.** M. Schwartz and T. C. Myers (Dept. of Biological Chem., Univ. of Ill. Coll. of Med., Chicago). *Anal. Chem.*, 1958, **30** (6), 1150–1151.—A simplified method is presented for the assay of enzyme systems in which reaction is accompanied by an alteration in the number of acid groups. Reaction is followed by a pH meter and the pH is kept constant by the addition of NaOH soln. from a syringe micrometer. The most important feature is that the necessary apparatus is generally available and that accurate and precise results are obtained. The essential features of the apparatus and procedure are described and illustrated. Enzyme activity - time curves are presented for the hexokinase and acetylcholinesterase systems. The method has other possible uses, *e.g.*, measurement of glycolysis under anaerobic and aerobic conditions. S. M. MARSH

See also Abstracts—**4173**, Separation of glucose and sorbitol. **4174**, Detection of ketohexoses. **4175**, Detection of heptoses. **4205**, Determination of aromatic nitro compounds in urine. **4208**, Determination of indole. **4287**, Determination of some alcohols and phenols. **4359**, Automatic recording in determination of amino acids. **4367**, Determination of carcinogens in tobacco smoke. **4380**, Micro-electrophoresis of protein fractions. **4381**, Apparatus for electrophoresis. **4382**, **4383**, Densitometer for blood-protein fractions.

Drugs

4272. **Volumetric determination of water in pharmaceutical preparations by the Karl Fischer method.** K. G. Krebs and J. Matern (Pharm. Dept., Univ. of Tübingen, Germany). *Dtsch. ApothZtg*, 1957, **97** (51–52); *Krankenhaus-Apotheker*, **7** (4), 29–32.—In this review, the preparation of the standard Karl Fischer reagent and of a modified, more stable reagent wherein the methanol is replaced by 2-methoxyethanol, is described. Details of titration apparatus and procedure are given, together with examples of the determination of H_2O in glacial acetic acid, fructose, Na tartrate and a cola extract with chocolate. (11 references.) A. G. COOPER

4273. **Note on specific rotation and temperature coefficient.** J. Rosin and C. J. Williams (Merck and Co., Rahway, N.J., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (3), 229.—The temp. coeff. of specific rotation is given for 16 medicinal chemicals. For some compounds it is $>$ 0·5% per degree; *e.g.*, colchicine shows $[\alpha]_D^{20} = -439{\cdot}7°$ and $[\alpha]_D^{30} = -409{\cdot}0°$. A. R. ROGERS

4274. **Study of the *Solanaceae*. Micro-determination of the alkaloids.** R. van Severen (Inst. de Pharm., Univ., Gand). *Pharm. Weekbl.*, 1958, **93** (5), 235–244 (in French).—Methods of determination are reviewed, with 40 references. The procedure given enables individual alkaloids to be determined, without destruction, in small samples of vegetable material. The accuracy is $\simeq \pm 5\%$. *Procedure*—Macerate the finely powdered drug (300 mg) with 0·02 *N* H_2SO_4 (7 ml) for 90 min. and filter. Add 10% aq. NH_3 (5 ml) and peroxide-free ether (50 ml) and shake for 3 min. Add tragacanth (1 g), shake for 1 min. and filter. Evaporate a 20-ml aliquot of the filtrate, add ether (2 ml), evaporate again, dissolve the residue in CO_2-free H_2O (1 ml) and titrate the combined alkaloids with 0·01 *N* H_2SO_4, with bromocresol green as indicator. Apply another portion of the ethereal filtrate to a strip of filter-paper impregnated with KCl and develop by the ascending technique with *n*-butanol - aq. HCl for 20 hr. Spray with modified Dragendorff reagent, measure the areas of the spots and calculate the relative concn. of the individual alkaloids by reference to calibration curves. The R_F values are—hyoscyamine, 0·85; hyoscine, 0·63; tropine, 0·34. A. R. ROGERS

4275. **Determination of alkaloids by chromatography on alumina. I. Total alkaloids of tincture of quinine.** K. Pfandl and J. Klotz (Chem.-Pharmazeut. Fabrik Müller, Göppingen, Germany). *Dtsch. ApothZtg*, 1958, **98** (2), 27–28.—The sample (5 g) is adsorbed on a column (500 mm × 15 mm) containing 10 g of Al_2O_3 and eluted with 40 ml of 86% w/w ethanol; the eluate is evaporated, dissolved in 10 ml of 95% w/w ethanol, diluted with 10 ml of water, titrated with 0·1 *N* HCl (methyl red), then diluted with 50 ml of water and re-titrated. Experiments with quinine and quinine sulphate demonstrated the accuracy of this procedure and showed the conventional extraction procedure to give high values for total alkaloids. A. G. COOPER

4276. **Separation and determination of reserpine, deserpidine and rescinnamine by partition column chromatography.** A. L. Hayden, L. A. Ford and A. E. H. Houk (Food and Drug Admin., Washington,

D.C., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (3), 157–159.—Moisten Celite 545 (20 g) with 20 ml of the lower layer of the solvent system *n*-heptane - $CHCl_3$ - morpholine - formamide (715:110:1:25) and pack in a column. Dissolve the alkaloids (≃ 1 mg) in $CHCl_3$ - methanol (3:1) (1 ml), mix with Celite (1 g) and transfer to the column. Elute with the upper layer of the solvent system at an initial rate of 5 ml in 3 min. Discard the first 100 ml of eluate; then collect successive fractions of 100 ml, 150 ml and 200 ml, which contain deserpidine (**I**), reserpine (**II**) and rescinnamine (**III**), respectively. The time required for complete elution is ≃ 6 hr. The separated alkaloids may be determined by u.v. spectroscopy; average recoveries are, for **I** 99%, **II** 97%, and **III** 95%.

A. R. ROGERS

4277. **The colorimetric estimation of digitalis glycosides.** D. H. E. Tattje (State Univ. of Groningen, Holland). *Pharm. Weekbl.*, 1958, **93** (5), 245–254 (in English).—Methods for the determination of digitalis glycosides are reviewed, with 42 references. It is shown that 2:4-dinitrophenyl phenyl sulphone (**I**) is more sensitive than picric acid, 3:5-dinitrobenzoic acid or *m*-dinitrobenzene as a colour reagent for the butenolide ring. *Procedure*—Dissolve the glycoside or aglycone in 96% ethanol (4 ml), mix with a 0·075% soln. of **I** in ethanol (5 ml), add 0·15 *N* aq. NaOH (1 ml) and measure the extinction at 600 mμ against a reagent blank in 0·5-cm cuvettes.

A. R. ROGERS

4278. **Estimation of digoxin and digitoxin in *Digitalis lanata*.** P. Tantivatana and S. E. Wright (Pharm. Dept., Univ. of Sydney, Australia). *J. Pharm. Pharmacol.*, 1958, **10** (3), 189–193.—Shake the powdered dried leaf with 20% ethanol, filter and extract the soln. with $CHCl_3$. Remove the $CHCl_3$ by evaporation and apply a soln. of the residue to formamide-impregnated filter-paper. Develop chromatographically with *iso*butyl methyl ketone - di*iso*propyl ether - formamide and determine digoxin and digitoxin colorimetrically with xanthhydrol reagent. Recoveries of these glycosides were within the range 95 to 100% for 20 to 60-μg amounts.

A. R. ROGERS

4279. **The suitability of the Indian frog (*Rana tigrina*) for the biological assay of tincture of digitalis.** A. K. Ghosh, R. K. Srivastava and J. N. Tayal (Tech. Development Estab. Lab., Kanpur, India). *J. Pharm. Pharmacol.*, 1958, **10** (3), 175–178.—The relationship between the logarithm of the dose of tincture of digitalis and the probit of the percentage mortalities among the Indian frog has been found to be linear. The results obtained by applying the B.P. 1953 two-and-two quantal response assay on the frog method were in fair agreement with those obtained by the use of guinea-pigs for four samples. The 95% fiducial limits of error of potency of the samples were within the B.P. limits. Frogs of suitable size are available only during the months July to November.

A. R. ROGERS

4280. **Determination of procaine in procaine penicillin.** M. K. Nayar, G. Ramana Rao and K. S. V. Soundaravalli [Antibiotics Res. Centre, Hindustan Antibiotics (Private) Ltd., Pimpni, Poona]. *J. Sci. Ind. Res., C, India*, 1958, **17** (2), 32–33.—A modified titrimetric method and an ion-exchange method are described. The two methods are comparable in accuracy to other standard methods. In the titrimetric method, procaine penicillin is directly treated with excess of H_2SO_4 to bind procaine and the free penicillin is removed by extraction with amyl acetate. The excess of acid is then directly titrated against alkali. This method is quicker than the official method and can be used as a routine procedure for process control. In the ion-exchange method, the components are separated from methanolic soln. on Amberlite IRA-400; procaine is eluted with methanol.

I. JONES

4281. **Assay of procaine penicillin in sesame oil by optical rotation.** B. A. Pappas and J. D. Duerr (Chas. Pfizer & Co. Inc., Brooklyn, N.Y., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (3), 215–217.—To assay procaine penicillin - aluminium monostearate - sesame oil suspension, shake the sample (3 g) with formamide (50 ml) and $CHCl_3$ (25 ml) and measure the optical rotation of the lower phase. The coeff. of variation calculated from 20 replicates is ≃ ± 0·6%, which is much less than those obtained by microbiological assay or by measuring the optical rotation of a heated $CHCl_3$ extract. The recovery is close to 100%.

A. R. ROGERS

4282. **Colorimetric determination of chloramphenicol cinnamate.** G. Machek and F. Lorenz (Anal. Lab., Biochemie G.m.b.H., Kundl, Tirol). *Sci. Pharm.*, 1958, **26** (1), 52–58.—Chloramphenicol cinnamate does not hydrolyse completely when treated with an enzyme as do other pharmaceutically important esters of chloramphenicol, and cannot be estimated by the methods normally used for these esters. A colorimetric method based on the reactivity of the nitro group, which has previously been applied to the parent compound, has been examined and is satisfactory if the prescribed procedure is used. The sample is reduced with zinc dust and HCl, diazotised and coupled with naphthylethylenediamine, the extinction being measured at 545 mμ. Cinnamic acid does not affect the determination, but palmitic acid (from the palmitate) must be removed. The determination of chloramphenicol cinnamate in syrups and 'chartae' (a preparation with cocoa powder and sugar) is described to illustrate the method.

S. M. MARSH

4283. **Determination of chloramphenicol in Chloromycetin ("otic") by ultra-violet spectrophotometry.** Yuki Yoneda (Shinagawa Plant, Sankyo Co., Shinagawa-ku, Tokyo). *Ann. Rep. Takamine Lab.*, 1957, **9**, 87–92.—In 0·1 *N* HCl, the u.v. absorption of benzocaine (**I**) (max. absorption 226 and 270 mμ) is much less than that of chloramphenicol (**II**) (max. 278 mμ); **I** and **II** may be determined spectrophotometrically by the use of two key bands at 270 and 290 mμ, with an average deviation < 1%. Propane-1:2-diol, the solvent for Chloromycetin ("otic"), does not affect the light absorption of **I** or **II**. The sample (1 ml) is diluted with 0·1 *N* HCl to make the **II** content ≃ 10 μg per ml and measured photometrically. The results agree well with those by bioassay.

K. SAITO

4284. **A shorter microbiological assay method for oxytetracycline and chlortetracycline.** N. László (Biol. Res. Lab., Hajdusági Gyógyszergyár, Debrecen, Hungary). *Nature*, 1958, **181**, 648–649.—The length of the incubation period of *Bacillus subtilis*, FDA 6633, used in the cup-plate assay method for antibiotics, can be shortened by adding

a growth factor to the spore suspension immediately before mixing with agar medium and pouring on to plates. Satisfactory results were obtained by using various concn. of DL-aspartic acid, folic acid, indol-3-ylacetic acid and lactose. G. S. ROBERTS

4285. **Determination of mixtures of steroid hormones in oily solution.** G. Tappi, E. Menziani Andreoli and E. Frea (Inst. de Chim. Pharm. et de Toxicologie, Univ. Turin). *Pharm. Weekbl.*, 1958, **93** (5), 231–234 (in French).—Transfer a 1% soln. of the sample in light petroleum (20 ml) to a chromatographic column of 60 to 100-mesh Florisil (10 g). Elute the solvent oil with light petroleum (100 ml) followed by light petroleum - $CHCl_3$ (3:1) (50 ml). Successively elute steroid esters with light petroleum - $CHCl_3$ (1:1) (100 ml), steroid ketones with $CHCl_3$ (100 ml), and steroid alcohols and phenols with $CHCl_3$ - methanol (1:1) (100 ml). Collect the separate fractions and determine the individual steroids colorimetrically or by u.v. absorption. Recoveries range from 94 to 97%.
A. R. ROGERS

4286. **Determination of urea injection with xanthhydrol.** Toru Hayashi and Takako Endo (Shinagawa Plant, Sankyo Co., Shinagawa-ku, Tokyo). *Ann. Rep. Takamine Lab.*, 1956, **8**, 136–138.—The pptn. of xanthylurea (Phillips and Pitt, *J. Amer. Chem. Soc.*, 1943, **65**, 1355) was applied to the determination of urea in injections containing NH_4^+. The reaction is completed within 7 hr.; NH_4^+ do not interfere. The sample (20 to 30 mg per ml) (1 ml) is mixed with glacial acetic acid and 5% xanthhydrol soln. in a mixture of methanol and acetic acid (1 + 4, by vol.), and filtered after 7 hr. The ppt. is washed with acetic acid and water, then transferred to a micro-Kjeldahl flask with ether, and the N is determined by the usual method.
K. SAITO

4287. **The assay of some official [Fr. P.] alcohols and phenols.** P. Mesnard and M. Bertucat (Fac. de Méd. et de Pharm., Bordeaux). *Pharm. Weekbl.*, 1958, **93** (5), 220–224 (in French).—To determine primary alcohols, secondary alcohols or phenols, mix the dry sample (0·2 to 0·5 g) with acetic anhydride - pyridine (1:3) (5 ml) and shake occasionally during 10 min. (for phenols), or 3 hr. (for primary alcohols), or 5 hr. (for secondary alcohols); add H_2O (50 ml) and titrate with 0·5 *N* NaOH. Satisfactory results were obtained with menthol, thymol, guaiacol, resorcinol and naphthols. To determine primary, secondary or tertiary alcohols, mix the dry sample with a mixture of 80% H_3PO_4 (5 drops), acetic anhydride (10 ml) and dioxan (20 ml), and shake occasionally during 24 hr. (for tertiary alcohols), or 6 hr. (primary or secondary alcohols); add pyridine (15 ml), wait 2 min., add H_2O (50 ml), wait 5 min. and titrate with 0·5 *N* NaOH. To determine terpin hydrate in preparations containing water, ethanol or other hydroxyl compounds, add a 0·1% aq. soln. of the sample (1 ml) to a mixture of 10% ammonium molybdate (1 ml) and H_2O (2 ml), add dioxan (1 ml) and conc. H_2SO_4 (1·5 ml) and compare the blue colour with that of a similarly treated standard (*cf.* Perelmann, *Pharm. Ztg, Berlin*, 1932, **77**, 1204).
A. R. ROGERS

4288. **Application of alcoholysis to the determination of some medicaments containing acetyl groups.** Mlle Pinguet (Lab. Nat. de Contrôle des Médicaments, Paris). *Pharm. Acta Helv.*, 1958, **33** (3), 114–119 (in French).—The action of ethanol in the presence of H_2SO_4 converts acetyl groups into ethyl acetate, which can be distilled off and determined by reaction with ethanolic KOH. The procedure given is suitable for the determination of samples of aspirin. Simple modifications make possible the determination of aspirin in tablets and cachets, and of 2-acetoxy-*m*-toluic acid, diacetylmorphine, acetylcholine hydrochloride and acetyl-*p*-aminosalol. Phenacetin gives recoveries of only 90%. *Procedure*—Mix the sample of aspirin (1 g) with 96% ethanol (100 ml) and conc. H_2SO_4 (5 ml) and distil through a 45-cm Vigreux fractionating column into a receiver containing *N* ethanolic KOH (15 ml) cooled in ice. Reflux the distillate for 30 min., cool and titrate with *N* H_2SO_4, with phenolphthalein as indicator. Simultaneously reflux *N* ethanolic KOH (15 ml) and titrate.
A. R. ROGERS

4289. **Resolution of binary mixtures [of drugs].** R. Bontemps (Serv. de Contrôle des Médicaments, 11 Rue Archimede, Brussels, Belgium). *Pharm. Weekbl.*, 1958, **93** (2), 61–71 (in French).—The resolution of binary mixtures of substances that have a similar method of colorimetric determination but different partition coefficients between $CHCl_3$ and an aq. buffer is carried out by a determination of a colorimetric factor which enables a datum of 20 mg to be established for a sample in terms of colorimetric units of one of the components. Various standard mixtures are made up to the 20-mg datum and extracted with $CHCl_3$, and the extract is determined colorimetrically. A regression line of composition against extinction of the extract is obtained. In the samples an overall colorimetric determination is made to enable a 20-mg datum to be taken, and this is then extracted with $CHCl_3$ and the extinction of the residue from evaporation of the extract determined. Substitution in the regression equation then gives the proportion of the components. Binary mixtures are analysed in the groups chlortetracycline, tetracycline, oxytetracycline; 5-methyl-5-phenylbarbituric acid, barbitone, phenobarbitone, methylphenobarbitone; and sulphadiazine, sulphamerazine, sulphamethazine, sulphanilamide, sulphathiazole. *Procedure for the tetracycline group*—To 5 ml of aq. procaine soln. (0·8 g per litre) are added 3 ml of aq. $NaNO_2$ soln. (0·4 g per litre), 15 ml of H_2O and 2·2 ml of *N* HCl. After 10 min., 5 ml of aq. 13·5% Na acetate soln. is added, followed by the soln. of the antibiotic (50 to 150 μg). The soln. is made up to 50 ml and the extinction is measured at 435 mμ. The partition with $CHCl_3$ is carried out between 100 ml of acetate buffer (50 ml of 0·1 *N* HCl, 25 ml of 13·5% aq. Na acetate soln. and 25 ml of water) and 100 ml of $CHCl_3$, by shaking for 10 min., decanting the $CHCl_3$ layer through a filter-paper, washing with 5 ml of $CHCl_3$ and distilling off the $CHCl_3$. The residue is taken up in ethanol and diluted with water to 100 ml. Similar procedures are used for the sulphonamide and barbiturate groups. The actual partition coefficients of the various compounds are quoted. The colorimetry of the barbiturate group is carried out by means of the u.v. absorption at 241 mμ, and of the sulphonamides by Bratton and Marshall's method (*J. Biol. Chem.*, 1939, **128**, 537).
E. J. H. BIRCH

4290. **Application of non-aqueous titration to drugs. I. Determination of lidocaine [lignocaine] hydrochloride injection.** Hiroshi Sakurai and Yoshio Sahashi (Shinagawa Plant, Sankyo Co., Shinagawa-ku, Tokyo). *Ann. Rep. Takamine Lab.*,

1956, **8**, 127–132.—The use of 0·05 *N* toluene-*p*-sulphonic acid (**I**) and 0·05 *N* $HClO_4$ for the titration of lignocaine (**II**) was examined in a mixture of ethanediol and *iso*propyl alcohol (1 + 1, by vol.) or of ethanediol and dioxan (1 + 1, by vol.) (indicator, methyl orange). No reaction takes place between $HClO_4$ and ethanediol; $HClO_4$ gives a more distinctive titration curve than **I**. Injection soln. of **II** (20 mg per ml) (1 ml) are mixed with water (4 ml) (1 g) and NaCl, made ammoniacal and extracted with $CHCl_3$ (4 × 5 ml). The $CHCl_3$ layer is washed with NaCl soln. (15%, 3 ml), then evaporated to dryness, and the residue is evaporated with ethanol (2 ml), dried over NaOH and dissolved in $CHCl_3$ (20 ml) for titration. K. SAITO

4291. **Bromimetric determination of 2-*n*-butylamino-1-*p*-hydroxyphenylethanol sulphate (Vasculat).** J. Blažek (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1958, **7** (1), 25–26.—The sample (≃ 25 to 50 mg) is dissolved in water, mixed with HCl and KBr, and a known volume of 0·1 *N* $KBrO_3$ is added in small portions. After 10 min. a 10% soln. of KI in 90% ethanol (10 ml) is added, and after another 10 min. the liberated iodine is titrated with 0·1 *N* $Na_2S_2O_3$ (starch as indicator). The accuracy is 99·5% to 101·1% for the substance, and 99·6% to 101·0% for injections.
J. VOLKE

4292. **Identification of drugs. IV. Antihistamines.** H. Baggesgaard-Rasmussen, J. Berger and K. Folting (Royal Danish School of Pharmacy, Copenhagen). *Dansk Tidsskr. Farm.*, 1958, **32** (2), 29–41.—The pure cryst. mono- or di-picrates of antihistamines can generally be prepared by the addition of an excess of 0·04 *N* picric acid soln. either to an ethanolic soln. of the salt or to a soln. of the free base in 0·2 *N* HCl. Detailed descriptions are given of these procedures, of modified procedures applicable to the prep. of the picrates of medrylamine (diphenhydramine) and pheniramine (prophenpyridamine), and of the method used for the extraction (by means of ether) of the base from tablets. Particulars tabulated for 20 antihistamines include trade names and formulae, published m.p. of the salts, the particular procedure suitable for the prep. of each of the picrates and (if necessary) for their recrystallisation, and the m.p. and equiv. wt. of the picrates. The equiv. wt. is determined by titration with 0·02 *N* $HClO_4$ in glacial acetic acid plus $CHCl_3$ soln. The m.p. (determined by the capillary-tube method) are reproducible, even when melting is accompanied by decomposition, and are reliable for the purpose of identification.
P. S. ARUP

4293. **Paper chromatography and electrophoresis of selected therapeutic agents. I. Paper chromatography of antihistaminic agents.** B. C. Cox, H. C. Heim and C. F. Poe (Coll. of Pharm., Univ. of Colorado, Boulder, U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (3), 226–227.—Values of R_F in the chromatography of 12 antihistamines on Whatman No. 1 paper pretreated with monosodium citrate are given for 6 solvent systems. The compounds are detected by the use of modified Dragendorff reagent. The preferred solvents are *iso*amyl alcohol - H_2O - citric acid (50:50:3, by wt.), *n*-butyl acetate - H_2O - amyl acetate (10:1:4, by vol.) and *iso*amyl alcohol - H_2O - ethyl acetate (10:1:3, by vol.). A. R. ROGERS

4294. **Separation of some phenothiazine derivatives.** A. Calò, A. Mariani and O. Mariani Marelli (Ist. Superiore di Sanità, Roma). *Pharm. Acta Helv.*, 1958, **33** (3), 126–131 (in French).—Promazine (**I**) can be separated from chlorpromazine (**II**), but not from related derivatives which do not contain chlorine, by paper electrophoresis. **I** is more mobile than **II**. Oxidation of **I** with iodic acid in H_3PO_4 soln. (*cf. Svensk Farm. Tidskr.*, 1956, 842) gives a colour with max. absorption at 515 mμ, which is less intense than that given by **II** with a max. at 526 mμ. A. R. ROGERS

4295. **Polarographic determination of pyrazinamide.** Masao Maruyama (Shinagawa Plant, Sankyo Co., Shinagawa-ku, Tokyo). *Ann. Rep. Takamine Lab.*, 1956, **8**, 122–127.—Pyrazinamide (**I**) exhibits a distinctive polarographic wave at pH 1 to 6, the $E_{\frac{1}{2}}$ value decreasing linearly with pH (− 0·38 V *vs.* the S.C.E. at pH 1·0 and − 0·76 V at pH 6·0). The wave height is proportional to concn. < 0·0006 *M* at pH 2·2. The error is ≃ 2%. For the separation of the wave of **I** from that of pyrazinoic acid, pH 9·0 is recommended, although the wave of **I** is less distinctive and **I** is subject to gradual hydrolysis. In the presence of isoniazid (**II**), both **I** and **II** can be determined polarographically at pH 2·2, the error being ≃ 5% for **II**. Deproteinised biological samples can also be analysed by this method. K. SAITO

4296. **Application of ion-exchange resins to analysis. I. Determination of pyrazinamide injection.** Shigeji Chiba (Shinagawa Plant, Sankyo Co., Shinagawa, Tokyo). *Ann. Rep. Takamine Lab.*, 1956, **8**, 132–136.—The ion-exchange separation of pyrazinamide (**I**) (≃ 3 mg per ml) and Na salicylate (≃ 200 μg per ml) was studied with Amberlite IRA-411 (Cl form). **I** passes through the column (diameter 10 mm, length ≃ 20 cm) (rate of flow 0·7 ml per min.) and is collected in the eluate with 100 ml of wash water, with only a negligible amount (< 15 μg) of salicylate. The eluate is made 0·4 *N* in HCl soln. (100 ml) and measured photometrically at 269 mμ (max. absorption of salicylate, 238 and 302 mμ). K. SAITO

4297. **Separative determination of pyrazinoic acid in a mixture with pyrazinamide.** Takeshi Kimura and Norioki Goto (Shinagawa Plant, Sankyo Co., Shinagawa-ku, Tokyo). *Ann. Rep. Takamine Lab.*, 1956, **8**, 141–147.—The complex (max. absorption 460 mμ) between pyrazinoic acid (**I**) (max. absorption 268 mμ) with $(NH_4)_2SO_4.FeSO_4$ (at pH 6·0) (Allen *et al.*, *Anal. Chem.*, 1953, **25**, 895) is stabilised by Fe^{2+} in an amount equiv. to 10 times that of **I**. Pyrazinamide does not form a complex with Fe^{2+}, but slightly increases the extinction near 460 mμ. An aq. sample soln. (< 140 μg of **I** per ml) (50 ml) is made pH 6·0 with 2% aq. NH_3 soln., then mixed with $(NH_4)_2SO_4.FeSO_4$ soln. (10%, 5 ml), and the extinction is measured at 460 mμ. The content of **I** is calculated from an empirical formula.
K. SAITO

4298. **Determination of quinoxaline and pyrazine-2:3-dicarboxylic acid.** Takeshi Kimura and Noribumi Sasaki (Shinagawa Plant, Sankyo Co., Shinagawa-ku, Tokyo). *Ann. Rep. Takamine Lab.*, 1956, **8**, 148–152.—The ultra-violet spectrophotometric determination of quinoxaline (**I**) (max. absorption 234·5 mμ) and pyrazine-2:3-dicarboxylic acid (**II**) (280 mμ) was studied in an intermediate for the synthesis of pyrazinamide. The extinction

is proportional to concn. for < 500 μg of **I** and < 2 mg of **II** per 100 ml at pH 5·10. Both **I** and **II** are simultaneously determined by two empirical formulae. K. SAITO

4299. **Determination of iodoform by photo-oxidation.** Sameer Bose (Mahakoshal Mahavidyalaya, Jabalpur, India). *Anal. Chem.*, 1958, **30** (6), 1137–1139.—The precise and simple method described is based on the quant. decomposition of iodoform which occurs when a soln. in ether - benzene is exposed to bright sunlight in the presence of air. An excess of $Na_2S_2O_3$ soln. is added before exposure to light and this reduces the iodine as it is liberated. The amount of $Na_2S_2O_3$ consumed is determined by back-titration with iodine soln. after addition of KI and starch indicator. Details of the procedure are given for the determination of iodoform in ethanolic soln. and in aq. suspension. Acetone may also be estimated after conversion into iodoform, and the procedure is described. The maximum amount of iodoform which can be estimated is 0·1 g and the results are accurate to within 0·5%. The advantages are speed, simplicity and applicability to the analysis of soln. of organic compounds that undergo quant. iodoform reaction. Disadvantages are interference by other iodine-substituted organic compounds, which must be eliminated before analysis, and the dependence on sunlight, although this might be overcome by the use of a mercury vapour lamp. S. M. MARSH

4300. **Polarographic determination of phenylmercury acetate and ethylmercury chloride.** Masato Kotakemori and Hisao Handa (Mishima Plant, Sankyo Co., Mishima, Shizuoka-ken). *Ann. Rep. Takamine Lab.*, 1956, **8**, 231–242.—In 0·1 *M* tetramethylammonium bromide soln. of pH > 9, phenylmercury acetate (**I**) exhibits a very low wave ($E_{\frac{1}{2}} = -0{\cdot}27$ V *vs.* the S.C.E.) with an almost const. wave height and does not cause interference in the determination of ethylmercury chloride (**II**) ($E_{\frac{1}{2}} = -0{\cdot}40$ V, 0·4 to 1·6 mg per 10 ml). In 0·2 *M* KNO_3 soln. of pH $\simeq 10$, both **I** and **II** give a reduction wave. The sum of **I** and **II** is proportional to the total wave height within the range 0·2 to 3 mg per 10 ml. Two 5-ml portions of the aq. sample soln. are made up to 10 ml with 0·01% gelatin soln., the pH being adjusted with Sørensen's buffer (pH 10), and the polarogram is recorded in the absence of O. K. SAITO

4301. **Rapid activity test of phenolic germicides with a pen-recording polarograph.** Hachiro Yamaguchi, Minoru Ohashi and Akira Nakatsuchi (Nitto Inst. of Chem. Res., Kamikizaki, Urawa). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1958, **61** (2), 168–172.—The measurement of the activity of various phenolic germicides was attempted by observing the change in wave height of the oxygen wave in a phosphate buffer containing glucose and bakers' yeast. The limiting current decreases linearly with time, the rate depending on the activity of the germicide. The phenol coeff. thus obtained was in good agreement with that obtained by the official culture method, both in the presence and the absence of organic substances such as biological excretions. The sample (xylenols, cresols and their chloro derivatives containing surface-active agents) is added to a mixture (100 ml) containing phosphate buffer [3·5% KH_2PO_4 and 3·5% $(NH_4)_2HPO_4$] (20 ml), glucose soln. (2%, 20 ml) and the yeast (1% suspension, 10 ml) while the polarogram is being recorded (scale, 36 mm per μA; mercury electrode, 2·27 mg per sec., 3·0 sec. per drop). The diffusion current at $-0{\cdot}4$ V *vs.* the S.C.E. is plotted against time. The minimum effective concn. is known from the concn. of the sample necessary to make the curve horizontal.
K. SAITO

4302. **Identification of some sulphonamides by fluorescence microscopy.** I. Tschudi-Steiner (Pharm. Anstalt der Univ., Basel). *Pharm. Acta Helv.*, 1958, **33** (3), 105–113 (in German).—The crystal form and intense fluorescence of the Schiff's bases of sulphonamides (**I**) with certain aldehydes are described. The following Schiff's bases can be used for identification of **I**—sulphadiazine with anisaldehyde (**II**) or *p*-hydroxybenzaldehyde (**III**), sulphasomidine with **III**, sulphadimidine with *p*-dimethylaminobenzaldehyde (**IV**), sulphamerazine with **II**, **IV** or salicylaldehyde. A. R. ROGERS

4303. **Identification of some antimalarial drugs.** E. G. C. Clarke (Dept. of Physiol., Royal Vet. Coll., London). *J. Pharm. Pharmacol.*, 1958, **10** (3), 194–196.—Crystal and colour tests are described for the identification of microgram quantities of 14 antimalarial drugs. A. R. ROGERS

4304. **Analytical study of solutions of medicinal calcium salts by chromatography on paper.** R. Monnet, F. Sabon, A. Viala and H. Grignon (Fac. de Méd. et de Pharm., Alger). *Pharm. Weekbl.*, 1958, **93** (5), 224–230 (in French).—One-dimensional paper chromatography is used to separate and identify 13 inorganic and organic acids commonly prescribed as soln. of the calcium salts. *Procedure*—Precipitate most of the Ca^{2+} by the addition of slightly less than the equiv. amount of 0·1 *N* oxalic acid. Develop a 10-μl aliquot containing 30 μg of acid by the descending technique on Arches 302 paper with either *n*-propanol - cineole - formic acid - H_2O (5:5:2:2) or *n*-propanol - methyl benzoate - formic acid - H_2O (6:4:2:2) or *n*-butanol - methyl benzoate - formic acid - H_2O (75:25:20:12) for 8 hr. The third solvent system is most generally suitable. Dry the chromatogram in warm air for 5 hr. and spray with a purple soln. of 0·04% bromophenol blue in alcohol; for boric acid, use a soln. containing also 10% of glycerol.
A. R. ROGERS

See also Abstracts—**3973**, Chemi-luminescent indicators in titrations. **4162**, **4305**, Determination of Hg in organic compounds. **4163**, Determination of alkoxyl groups. **4189**, U.v. absorption analysis of quaternary ammonium compounds. **4190**, Murexide test for purines. **4191**, Polarographic study of nitrogen mustards. **4206**, Determination of camphor. **4219**, Analysis of surface-active agents. **4240**, Determination of adrenaline. **4241**, **4242**, Determination of adrenaline and noradrenaline. **4225**, **4226**, Determination of sterols in wool-fat. **4381**, Electrophoresis of *Strychnos* alkaloids.

Food

4305. **Determination of small quantities of mercury in organic combination in foodstuffs and pharmaceutical preparations.** J. A. Gautier and F. Pellerin (Fac. de Pharmacie de Paris, France). *Prod. Pharm.*, 1958, **13** (3), 149–152.—The mercury compound is decomposed with zinc and NaOH. The mercury forms an amalgam with the zinc,

which is dissolved in acid, and the Hg is determined iodimetrically or colorimetrically. Dilute an amount of sample containing 50 mg (iodimetric) or 25 μg (colorimetric) of Hg to 50 ml with water, add 5 g of pellet NaOH, 1 g of zinc powder and a few drops of octyl alcohol, and boil gently under reflux for 5 hr. When cold, wash the amalgam by decantation, treat it with 20 ml of dil. HNO_3 (1:1), and, after a few minutes in the cold, boil gently under reflux till dissolution is complete. Cool. For the iodimetric procedure, after destroying nitrites in the soln. by boiling with urea, precipitate the Hg by boiling with formaldehyde soln. in the presence of KI and NaOH, acidify, add an excess of 0·1 *N* iodine and back-titrate in the usual way. For the colorimetric procedure, convert the Hg into Hg^{2+} and determine with dithizone, reading the extinction at 500 mμ. Results for five mercurials, dissolved in various substrates, show good agreement between the present procedures and the International Pharmacopoeial method.

R. E. Essery

4306. **The determination of sugar in sugar beets. I.** W. H. Parker. *Int. Sugar J.*, 1958, **60**, 102–105.—Methods developed by the British Sugar Corporation in the past seven years for the preparation of samples for analysis are described and compared in detail, with illustrations of the machines used. The standard reference method has been the chopping and grinding of the whole sample, with first a "root cutter" and then a mincing machine, by which a 25-lb sample is mixed, quartered, etc., to reduce it to approx. 5 lb which is analysed by hot-water digestion, or, if a macerator is also used, by cold-water digestion. Results with a multiple-saw machine, giving a "brei" by a repeated rasping process, were very close to those of the reference method; the design of this machine had required close attention to details such as saw and carriage speed, tooth size, quality of steel used, etc., in order to give reliable analytical results. Methods tested with sliced roots or cossettes were the use of a top-drive macerator with screen of varying aperture, and later of an "Atomix" macerator, now adopted officially. For the latter, sampling by means of a "wad punch" type of sampler enabled rapid preparation of aliquots to be made.

II. The preparation of samples for analysis. W. H. Parker. *Ibid.*, 1958, **60**, 132–135.—A detailed discussion is given of the rate of cutting by a saw blade rotating in front of the hollowed-out quadrants of the beet carrier in a "multiple saw" machine for sampling beet, taking into account the need to avoid any crushing action and to prepare samples with a constant ratio of solid to liquid. The design of saw blade and the type of steel required in order to reduce risks of fracture and wear are also fully considered in relation to stresses occurring in operation. Sugar Ind. Abstr.

4307. **The effect of basic lead acetate solution upon the optical rotation (polarisation) of solutions of sucrose, laevulose [fructose] and dextrose [glucose] and of various mixtures of these solutions.** J. G. N. Gaskin and R. J. Mesley. *Int. Sugar J.*, 1958, **60**, 65–71.—Measurements of optical rotation were made after addition of 0 to 6·0 ml of basic Pb acetate soln. to 20 ml of a "normal" soln. of sucrose, 7 concn. of fructose, 3 concn. of glucose and to mixtures of sucrose and fructose, glucose and fructose, or of all three sugars. The results are plotted in various ways. The sucrose soln. and mixtures of sucrose with the other sugars all show an initial drop in polarisation (min. with 0·6 ml of lead soln.), a rise to the initial value with about 1·0 to 1·4 ml of lead soln. and a steady increase thereafter. The significance of these results in relation to correction of raw sugar polarisations for lead effect is discussed. Sugar Ind. Abstr.

4308. **Polarographic estimation of starch and its application in flotation.** Shiou-Chuan Sun, D. L. Love and R. T. Holzmann (Coll. of Min. Ind., Pennsylvania State Univ., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1074–1076.—To the sample add conc. HCl to give a concn. of 5 to 450 mg per litre. Boil for a predetermined length of time and re-adjust the vol. with const.-boiling HCl. Remove O by bubbling N for 10 min. and record the polarogram from − 0·23 to − 0·60 V *vs.* the S.C.E. Determine the starch content from calibration curves. The method has been applied to three starches and is believed to be applicable to some other starches and carbohydrates. Interference by Cu and Ni is eliminated by pptn. with thioacetamide.

K. A. Proctor

4309. **Paper-chromatographic determination of phosphates used in meat products. I. Qualitative detection of ortho-, pyro- and poly-phosphates.** M. S. Pohja, E. Aalto and F. P. Niinivaara (Osuusteurastamojen Tutkimuslaitos, Hämeenlinna, Finland). *Z. LebensmittUntersuch.*, 1957, **106** (6), 441–451.—Chromatographic methods and various special flow solvents were studied to find a quick means of isolating and identifying ortho-, pyro- and poly-phosphates. Best results were obtained with the round-filter process and *iso*-propyl alcohol - trichloroacetic acid (20%) - water - aq. NH_3 (0·880) (70:20:10:0·3) with 50 μg of phosphate. For the colouring of the phosphate zones ammonium molybdate soln. was used followed by benzidine soln. - aq. NH_3. The chromatogram was dried at room temp. If a mineral acid is used in place of trichloroacetic acid or other org. acid, a temp. below 25° (5° to 10°) is necessary. To extract the phosphates, *e.g.*, from sausage, the crushed mass is mixed with trichloroacetic acid and the soln. is pressed out. S.C.I. Abstr.

4310. **Influence of various clarifying agents on the polarimetric determination of starch according to Ewers.** S. Zelenka and B. H. Kopriva. *Stärke*, 1957, **9** (12), 247–250.—Clarifying agents to precipitate non-starch substances are required for Ewers' polarimetric determination of starch (*Z. öffentl. Chem.*, 1908, **14**, 150; 1909, **15**, 8). The influence of some commonly used agents was investigated. (*i*) Soln. (30%) of Pb acetate and basic Pb acetate had no value as clarifying agents. (*ii*) Soln. (3%) of tungstophosphoric acid as well as sodium and ammonium molybdates caused some diminution of $[\alpha]_D$ of pure starch soln., probably owing to slight pptn. of starch. (*iii*) Theoretical values of $[\alpha]_D$ were obtained by the use of the Carrez reagent. Starch (1 g) is dispersed in 0·42% HCl (50 ml) and the container immersed in boiling water for 15 min. The soln. is cooled and the reagent, 30% $ZnSO_4$ soln. (1 ml) followed by 15% $K_4Fe(CN)_6$ soln. (1 ml), is added. The soln. is made up to 100 ml, filtered and analysed polarimetrically in a tube of length 20 cm. Comparisons were made by determining the dry substance in commercial starch by this method and by oven drying. Results agreed to ± 0·01%. E. Dux

4311. **Determination of solids content of ice-cream by irradiation with infra-red light, with the use of filter-paper and aluminium foil.** J. Kottász (Städt. Anstalt f. Chemie und Lebensmitteluntersuchung, Budapest). *Mitt. Lebensmitt. Hyg., Bern*, 1958, **49** (2), 121–126.—A method is described for drying ice-cream on filter-paper. Sheets of paper (12 cm × 12 cm) are laid in an open envelope of aluminium foil and exposed to an infra-red lamp (250 W) at 17 cm distance for 3 min. The paper is then completely wrapped in the foil and weighed. The ice-cream is then spotted on the paper as individual drops from a pipette, obtaining the total amount by weighing the pipette before and after the application. The paper is exposed to the lamp for 15 min., wrapped and weighed. This procedure reduces exposure of the dried film to atmospheric humidity as well as eliminating the cooling period in a desiccator. A complete determination takes 34 min. E. Dux

4312. **Acidity relations in beverages. I. Potentiometric determination of titratable acidity.** A. Schaller and F. Paul (Bundeslehr- u. Versuchsanstalt f. Chem. Ind., Vienna). *Mitt. Wein- u. Obstbau, Wien, A*, 1958, **8** (2), 81–93.—The literature of the subject is reviewed and discussed. Results obtained for a large number of wines, fruit and vegetable juices, and fruit beverages show wide variations in the potentiometric equivalence points for the determination of titratable acidity. Satisfactory values can be obtained only by the potentiometric determination of inflection points; the choice of one or more such conventional end-points remains to be decided. P. S. Arup

4313. **Contributions to the technique of the determination of citric acid. II. Behaviour of triethyl citrate.** K. Täufel and U. Behnke. *Ernährungsforschung*, 1958, **3** (1), 52–57.—An explanation for the increases in the citric acid content of certain natural substrates found after boiling with dil. aq. KOH soln. (*Ibid.*, 1957, **2**, 758) may possibly be found in the observation that triethyl citrate is readily hydrolysed under similar treatment. Corresponding decreases in the apparent citric acid content of bakers' yeast are probably due to the destruction by KOH of substances simulating citric acid in its determination as pentabromoacetone. P. S. Arup

4314. **Range of validity of simplified method of calculation for the proportion by weight 20°/20° or 20°/4° for the determination of must weight, alcohol and extract content in grape must and wine by the pycnometer method.** P. Böhringer (Landes-Lehr- u. Forschungsanstalt f. Wein- und Gartenbau, Neustadt a.d.W.). *Z. LebensmittUntersuch.*, 1957, **106** (6), 455–460.—In this mathematical discussion, based on practical findings, simplified equations are developed in which pycnometer constants are used, thereby speeding the calculations. Temp. of 20° and 4° are considered. S.C.I. Abstr.

4315. **The chemical differentiation of natural and sweetened wines.** H. Rentschler and H. Tanner (Eidg. Versuchsanstalt, Wädenswil, Switzerland). *Mitt. Lebensmitt. Hyg., Bern.*, 1958, **49** (1), 10–14.—A method for the recognition of artificially sweetened wines is described, which has as its basis the acceptance of a constant K = (glycerol × butane-1:3-diol)/ethanol, expressed as g per litre (*cf.* Rebelein, *Weinblatt*, 1957, **52**, 768). This constant for natural wines ranged from 7×10^{-6} to 9×10^{-6}, and for artificial wines was $< 4{\cdot}5 \times 10^{-6}$. S. Baar

4316. **New technique for the micro-determination of metals in wines by previous adsorption with resins. Iron determination.** E. Gálvez and J. M. Garrido (Juan de la Cierva de Investigación Técnica, Madrid). *Rev. Cienc. Apl.*, 1957, **11**, 514–520.—The sample of wine (10 to 25 ml) is shaken with 3 g of Permutit Q ion-exchange resin in a separating funnel, whose outlet is packed with glass wool. The resin is washed with twice-distilled water until the pH is 7, then eluted (× 5) with 3 *N* HCl. The combined eluates are diluted to 100 ml, and two 10-ml aliquots are taken. To one is added 6 ml of a 3 *N* KSCN soln. in aq. acetone, to the other 1 ml of bromine water and then the same amount of KSCN soln., and the Fe^{III} and the total Fe are measured, respectively, in a Beckman C photometer with a blue filter (440 mμ). The method has been checked with a synthetic wine containing citric, tartaric, phosphoric and lactic acids, ethanol, glycerol, $CaSO_4$, K_2SO_4 and $FeCl_3$ (25 mg of Fe per litre), and gave as an average of 6 analyses a value of 24·934 mg of Fe per litre, compared with 24·15 mg per litre found by calcination followed by the conventional determination of Fe. With three natural wines (white, sweet and red) the average results found by the two methods were 11·6, 8·04 and 2·56, and 11·04, 8·38 and 2·7 mg of Fe per litre, respectively. Ferric iron (20 mg per litre) was added to a white and a sweet wine, and 2·5 mg per litre to a red one, by a procedure that avoids the pptn. of ferric phosphate, and the measurements of the new concn. showed average errors of 0·38, 0·20 and 0·12 mg per litre, respectively. The method enables Fe^{II} to be determined by difference, except with red wines, when a slight violet coloration remains in the eluate which, however, is destroyed by the oxidation. H. Friedmann

4317. **Validity of some methods for controlling the purity of olive oil.** M. Vitagliano (Naples Univ., Italy). *Olii Min.*, 1958, **35** (3), 73–79.—Various modifications of the Bellier test for detecting arachis oil in olive oil have been examined, but none is completely satisfactory, difficulties arising from the range of values found for genuine olive oil from different sources and from the presence of "rectified B" and re-esterified oleins. Methods dependent on the detection of arachidic acid need to be quantitative because of the small amounts found in natural olive oils. Other modifications of the Bellier test for detecting "rectified B" in olive oil are complicated by re-esterified oleins and by products from extracted oils; the colorimetric reaction with $AgNO_3$ is unsatisfactory. L. A. O'Neill

4318. **The catalytic esterification of olive oil fatty acids and their detection in olive oils.** A. Massarotti (Canton Lab., Lugano, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1958, **49** (1), 15–29.—The basic principles used in the large-scale esterification of olive oil fatty acids are described, and analytical details are given for the quant. evaluation of the esterification products. Saponification with alcoholic KOH, slight acidification with dil. acetic acid and cooling makes the identification of an admixture of extraction oils or arachis oil possible. The usefulness of the colour reactions summarised by Ciusa (*Boll. Lab. Chim. Prov.*, 1951, 105) is

emphasised. It was also found that olive oils contained only 0·3 to 0·7% of monoglycerides, while esterified oils had 5·0 to 8·0%. Esterified oils also gave acetyl numbers of at least 12 compared with 4·4 to 8·0 for refined olive oils. Details of a modification for the determination of hydroxyl numbers are given. Monoglycerides are separated chromatographically and determined quantitatively by oxidation with $HIO_4.2H_2O$. Aniline points were obtained by a recognised method. The presence of trace metals used for catalysis was established chromatographically. S. BAAR

4319. **Vapour-phase chromatography of methyl esters of fatty acids and their quantitative determination by automatic coulometry.** A. Liberti, G. P. Cartoni and U. Pallotta (Inst. Anal Chem., Univ. Messina). *Ann. Chim., Roma*, 1958, **48** (1), 40–49.—The acids obtained by saponifying the sample of fat are extracted and converted into the methyl esters, which are then separated by vapour-phase chromatography. The individual esters are identified and determined by automatic coulometry. A detailed description of the apparatus is given. The method may be of value for determining the composition of fats and also for detecting adulteration. A. G. COOPER

4320. **Separation of polyunsaturated fatty acid methyl esters by gas chromatography.** C. H. Orr and J. E. Callen (Procter and Gamble Co., Cincinnati, Ohio, U.S.A.). *J. Amer. Chem. Soc.*, 1958, **80**, 249.—The esters of caprylic, capric, lauric, myristic, palmitic, palmitoleic, stearic, oleic, linoleic, linolenic, arachidic and erucic acids have been separated on a column of 30% Reoplex 400 Plasticizer, with helium as carrier gas at 240°. The retention volumes for the esters are quoted. C. A. SLATER

4321. **Paper chromatography of sterols in animal and vegetable fats.** J. C. Riemersma and W. Stoutjesdijk (Reichsuntersuchungsanstalt f. Molkereiprodukte und Nahrungsfette, Leiden, Netherlands). *Mitt. Lebensmitt. Hyg., Bern*, 1958, **49** (2), 115–120.—Paper chromatography has been found useful for detecting the presence of animal fats in vegetable fats. The sterols are isolated by saponification of the fat and subsequent pptn. with digitonin soln. They are then acetylated and finally saponified to free sterols. This procedure enables total sterols to be determined concurrently with the m.p. of their acetates. Stigmasterol is isolated by preparing the nearly insol. tetrabromostigmasteryl acetate (**I**). Chromatographic separation is preferably carried out by the method of Sulser and Högl (*Anal. Abstr.*, 1958, **5**, 2404) with Whatman No. 1 paper impregnated with liquid paraffin, and development with ethanol (95%) (descending technique) for 24 hr. Sterols are detected with molybdophosphoric acid. Stigmasterol is chromatographed as **I** and detected with $SbCl_3$. It is essential to use only freshly prepared soln. By using this procedure the presence of 5% of cholesterol was detected in pure sterols, and the presence of 5% of animal fat was detectable in vegetable fat. E. DUX

4322. **New method for the chromatographic separation of vitamin-A alcohol, acetate and palmitate.** G. Rindi (Physiologisch-Chem. Inst., Univ. Basel, Switzerland). *Intern. Z. Vitaminforsch.*, 1957, **28** (1–2), 191–192 (in Italian).—Prepare a chromatographic column (24 cm × 1 cm) of powdered polyethylene previously washed with acetone, benzene and acetone in succession. Displace the acetone by 50% aq. acetone and add the sample (containing 40 to 100 μg each of vitamin-A alcohol, acetate and palmitate) dissolved in acetone (1 or 2 ml) and an equal vol. of water. Wash the column with 50% acetone (50 or 60 ml) with the aid of N under pressure. Elute the vitamin-A alcohol in 91 to 94% recovery with 60% aq. acetone (60 to 100 ml), vitamin-A acetate in 96 to 98% recovery with 80% aq. acetone (50 to 80 ml), and vitamin-A palmitate in 79 to 82% recovery with 100% acetone. A. R. ROGERS

4323. **Chromatographic separation of α-, β-, γ- and δ-tocopherols.** A. Mariani and C. Vicari (Ist. Superiore di Sanità, Roma). *Pharm. Acta Helv.*, 1958, **33** (3), 120–125 (in French).—The azo compounds formed by the coupling of β-, γ- and δ-tocopherols with diazotised *o*-dianisidine at pH 11 can be separated by chromatography on alumina. *o*-Dianisidine cannot be coupled with α-tocopherol. *Procedure*—Dissolve the sample (containing a few mg of tocopherols) in ethanol (3 ml) and add 2% aq. Na_2CO_3 soln. (7·5 ml) and a soln. of diazotised *o*-dianisidine (1 ml). Shake the mixture and allow it to stand for 5 min. at room temp. Add anhyd. Na_2SO_4 (0·5 g) and extract with light petroleum. Apply the extract to a column of activated alumina (12 g) and develop with light petroleum, a 1% soln. of ether in light petroleum and a 20% soln. of ether in light petroleum, in succession. The three fractions of eluate contain, respectively, the red - brown azo derivatives of γ- and β-tocopherols and the blue - purple azo derivative of δ-tocopherol. A. R. ROGERS

See also Abstracts—**3973**, Chemiluminescent indicators in titrations of acidity. **4012**, Determination of ^{90}Sr in milk. **4174**, Detection of ketohexoses. **4180**, **4181**, Determination of organic acids. **4183**, Determination of malic acid. **4237**, Determination of riboflavine. **4246**, Reagent for fatty acids. **4348**, Determination of phosphorodithioate residues in olive oil and fruits.

Sanitation

4324. **Evaluation of air-borne particulates in atmospheric pollution studies.** M. Katz, H. P. Sanderson and M. B. Ferguson (Dept. of Nat. Health & Welfare, Ottawa, Canada). *Anal. Chem.*, 1958, **30** (7), 1172–1180.—The relation between the absorbance values of filtered deposits from air samples and the mass concn. or C content of particulate matter in the atmosphere was studied under various meteorological conditions. The relationship between wt. concn. and absorbance was analysed and the data satisfied the equation $W = aD_b$, where W is the wt. of the deposit, D is the absorbance of the stain × 100 and a and b are constants. In 24-hr. runs, each individual run complied with this equation, but the values of the constants varied from day to day especially if there was a sharp change in weather conditions. Frequent calibration was therefore essential for successful application. G. P. COOK

4325. **Determination of trace quantities of hydrocarbons in the atmosphere.** E. R. Quiram and W. F. Biller (Esso Res. and Engng Co., Linden, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (7), 1166–1171.—The mass-spectrometer method is based on a concentration technique in which the fixed gases

in the sample, such as O, N and H, are pumped off at the temp. of liquid N whereas the hydrocarbons are not. Water and CO_2 are removed under high vacuum with the aid of suitable absorbents. Methane cannot be determined because it is not retained at the operative temp. Synthetic samples containing as many as 11 different hydrocarbons in air gave recoveries of $\simeq$ 100% at the 100 p.p.m. level. G. P. COOK

4326. Determination of small amounts of acetylene in air with silica gel treated with liquid oxygen. Eizo Yasui and Hiroshi Suzuki (Res. Lab., Nagoya Plant, ToaGosei Chem. Ind., Minato-ku). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1958, **61** (2), 176–179.—Whilst chlorine gas increases the intensity of the colour formed by the reaction between Ilosvay reagent and acetylene, SO_2, NO_2, CH_4, CO_2 and NH_3 decrease it. These are all removed by bubbling the sample gas through conc. H_2SO_4 (100 ml) and pyrogallol soln. (10% in 20% KOH) (150 ml). For the collection of acetylene (0·3 to 1·5 mg per litre) from air (< 50 litres), the gas is passed (500 cu. cm per min.) through 4 dehydrating tubes (each containing 60 g of silica gel) into a silica gel layer ($\simeq$ 20 g) immersed in liquid oxygen (> 150 ml) free from acetylene. Most of the liquid oxygen is removed by a current of N (200 to 300 cu. cm per min.) and then the remaining liquid oxygen and acetylene are caused to react with Ilosvay reagent after passage through H_2SO_4 and pyrogallol. The error is 5 to 10%. (*Cf.* Matsui *et al.*, *Anal. Abstr.*, 1958, **5**, 554.) K. SAITO

4327. Fixation of atmospheric carbonyl compounds by sodium bisulphite. K. W. Wilson (Dept. of Engng, Univ. of California, Los Angeles, U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1127–1129.—From 0·3 to 0·5 p.p.m. of formaldehyde and acetone in the atmosphere can be determined by a slight modification of Goldman and Yagoda's procedure (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 377). The two impingers containing 1% aq. $NaHSO_3$ soln. are cooled at 0°, whilst the air is drawn through them at a rate of 2 litres per min. This ensures quant. trapping of acetone and of aldehydes up to C_4, and trapping of some ethyl methyl ketone. The excess of $NaHSO_3$ is removed with 0·5 *N* iodine, and the aldehyde - bisulphite is titrated with 0·005 *N* iodine after decomposition with an acetate - carbonate buffer. Accuracy and precision are improved, but the comparatively low sensitivity and the long sampling time ($\simeq$ 1 hr.) make the method unattractive for routine control. W. J. BAKER

4328. Determination of carbon from household fuel in town refuse. F. C. Gerretsen and W. A. C. Campen (Inst. v. Bodemvruchtbaarheid, Groningen, Netherlands). *Chem. Weekbl.*, 1958, **54** (12), 155–156.—The easily destructible org. matter is oxidised by Scharrer - Kürschner reagent [trichloroacetic acid (25 g) and HNO_3 (sp. gr. 1·4) (62 ml) diluted to 1 litre with 70% acetic acid]. The residue is filtered off, washed with water and acetone and dried. Any cellulose present is dissolved from the residue with Schweitzer's reagent. The washed and dried residue is weighed, heated for 2 hr. at 900° and again weighed, the difference being calculated as carbon. P. HAAS

4329. Direct spectrophotometric determination of chloride ion in water. P. W. West and H. Coll (Coll. Chem. and Phys., Louisiana State Univ., Baton Rouge). *J. Amer. Wat. Wks Ass.*, 1957, **49** (11), 1485–1492.—Chloride at a concn. of a few milligrams per litre can be determined by measuring the absorption at 353 mμ of about 2·5 ml of water in 7·4 ml of reagent comprising 0·014 *M* ferric perchlorate in 12 *N* $HClO_4$. Interference from other ions is either slight or non-existent. The accuracy was $\pm$ 1·2% for soln. containing 12·5 mg of Cl^- per litre compared with $\pm$ 1·1% for the Mohr method and $\pm$ 1·4% for the mercuric nitrate method (25 replicate tests). Treatment with $Al(OH)_3$ is generally adequate to remove coloured contaminants in natural waters. Occasionally decolorisation with $KMnO_4$ and oxalate may be needed. The method is reliable, very simple and particularly suitable for routine analysis. G. HELMS

4330. Determination of iodine in natural waters. E. N. Belyaeva. *Gigiena i Sanit.*, 1957, (6), 72–74; *Ref. Zhur., Khim.*, 1958, Abstr. No. 21,195.—Neutralise the sample of water with 0·1 *N* K_2CO_3 till weakly alkaline to phenolphthalein, evaporate to 20 or 25 ml and distil into a receiver containing 1 ml of 0·1 *N* Na_2SO_3 and 1 ml of 0·1 *N* K_2CO_3. To the distillation flask add a saturated $K_2Cr_2O_7$ soln. (10 ml) and H_2SO_4 (1 : 1, 10 ml), boil for 15 or 20 min., then add in small portions $\simeq$ 20 ml of a saturated oxalic acid soln. (to reduce IO_3^-) and continue the distillation of iodine for a further 20 or 25 min. For the iodimetric determination of iodine, evaporate the distillate to 5 or 10 ml, add 0·25 *N* $KMnO_4$ dropwise to a pink colour, warm for 5 min. on the water bath, neutralise to litmus with 2 *N* H_2SO_4, warm for a further 5 min., add a few drops of *N* $NaNO_2$ (to destroy excess of $KMnO_4$) and *M* thiourea (to destroy excess of nitrite), evaporate to 2 or 3 ml, cool, add 0·1 ml of a 0·2% soln. of KI and titrate the liberated iodine with 0·001 *N* $Na_2S_2O_3$ in the presence of starch. For the colorimetric determination of iodine, evaporate the distillate to 3 or 4 ml, transfer to a 10- or 15-ml colorimetric tube, add *N* H_2SO_4 till acid to litmus, add water to 5 ml, 0·1 ml of $CHCl_3$ and 0·5 ml of *N* $NaNO_2$, mix, and after 10 min. compare the colour of the $CHCl_3$ layer with that of a standard series of soln. prepared analogously. The method described for separating iodine is considerably more rapid and easier to carry out than other methods. C. D. KOPKIN

4331. Rapid determination of sulphide sulphur in water by means of a detector tube. Yoshitaka Kobayashi (Fac. of Engng, Yokohama Univ., Minami-ku). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1958, **61** (1), 48–52.—Dried silica gel (40 to 60 mesh, 100 g) is mixed with Pb acetate soln. (0·5%, 100 ml) and dried to adjust the water content to $\simeq$ 30%. The product (0·2 g) is packed in a glass tube (inner diameter 2 mm) and kept sealed. One end of the detector is immersed in the sample soln. (mineral water, industrial waste water) for 3 min. The length of the coloured layer increases with the content of S (2 to 1000 p.p.m.) and is independent of the pH. The amount is determined by reference to an empirical table. The error is $\simeq$ 10%. No interference results from SO_4^{2-} (< 15 g per litre), CrO_4^{2-} (< 0·05 g), Fe^{2+} (< 2 g), Cl^- (< 25 g) and CO_3^{2-} (< 40 g). K. SAITO

See also Abstracts—**4203**, Detection of N-2-fluorenylacetamide in dust and air. **4301**, Activity test of phenolic germicides. **4376**, Detection of nerve gases in air. **4377**, Detection of toxic agents in air.

Agriculture and Plant Biochemistry

4332. Condensed direct-current arc excitation for spectrochemical analysis of plant materials. H. E. Braun (Agric. College, Guelph, Ontario, Canada). *Anal. Chem.*, 1958, **30** (6), 1076–1079.—The Ca, Mg, P, Fe, B, Mn and Cu in plant tissues can be quant. determined from one established set of standard curves. The plant ash in acid soln. is impregnated into powdered graphite held in a cratered electrode, which is then dried and excited in a condensed d.c. arc. Standard deviations (48) of spectrographic results from chemical results were calculated and in only 11 instances did this exceed 10% of the mean of the chemical results. The coeff. of variation on 10 replicates of a sample of red clover ranged from 3·5 to 8·2% for individual elements.

K. A. PROCTOR

4333. Determination of glutamine and asparagine in plant sap. A. Niemann (Landwirtsch. Forschungsanst. Büntehof, Hannover, Germany). *Naturwissenschaften*, 1958, **45** (1), 12.—Glutamine is converted quant. into glutamic acid by heating in a sealed tube for 2 hr. at 100° in the presence of *N* HCl. Asparagine is similarly converted into aspartic acid if 2 *N* HCl is used. Both hydrolysed and unhydrolysed material is subjected to paper chromatography (or electrophoresis) together to make allowance for peptides that are broken down during the hydrolysis. The quant. assay is carried out on the chromatograms or electropherograms after spraying with ninhydrin, stabilising the resulting colour with copper and photometric evaluation at 510 mμ of the eluted pigment. From the differences between the values of the unhydrolysed and hydrolysed material the content of glutamine and asparagine is calculated.

E. KAWERAU

4334. Identification of non-volatile acids in plant tissues by paper chromatography. Chia-Hsiang Hsu. *Acta Chim. Sinica*, 1957, **23** (3), 201–209.—The R_F values of seven organic acids in amyl alcohol - butanol - formic acid - water mixtures were determined; tartaric, citric, malic, oxalic, maleic, succinic and fumaric acids were examined. The values generally agreed with those normally found except for oxalic acid which left long trails and these were not eliminated by increased concn. of the swamping acid. A modified method is described for the determination of org. acids in plant tissues.

S.C.I. ABSTR.

4335. Mass isotope dilution assay for gibberellic acid. B. H. Arison, O. C. Speth and N. R. Trenner (Merck Sharp & Dohme Res. Lab., Rahway, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1083–1085.—The method is applicable to fermentation broths and involves the addition of a known wt. of tracer, which is prepared by treating gibberellic acid with 85% deuteroacetic acid at 56° in the presence of a platinum catalyst. This is followed by qual. isolation of a pure isotopically mixed specimen, combustion of the isolate and i.r. determination of the D in the water so produced. The accuracy is about ± 4%.

K. A. PROCTOR

4336. Quantitative determination of phytol. O. Hromatka and L. Stentzel (Chem. Inst. I, Univ., Vienna). *Monatsh.*, 1958, **89**, 54–60.—Two methods were used and full details of the techniques are given. (*i*) Reichstein's gravimetric method (*Helv. Chim. Acta*, 1926, **9**, 799), originally intended for the determination of lower alcohols, was successfully adapted for phytol. It consists in the esterification of phytol, in pyridine medium, with 3:5-dinitrobenzoic acid and subsequent treatment of the ester with 1-naphthylamine. A compound of the composition $C_{37}H_{51}O_6N_3$ is formed quant., 1 g of which is equiv. to 0·4678 g of phytol. (*ii*) The colorimetric method of Masuyama and Hamada (*J. Chem. Soc. Japan*, 1949, **70**, 198, 232; 1950, **71**, 47), also intended originally for alcohols, and based on the formation of red urethanes by the action of 4-*iso*cyanatoazobenzene, was applied to phytol. Various side products are formed from which the urethane is separated by chromatography on alumina. The accuracy is 2%.

A. TESSLER

4337. Partition separation of carotenoids by silica - methanol columns. A. E. Purcell (U.S. Fruit and Vegetable Products Lab., Weslaco, Texas). *Anal. Chem.*, 1958, **30** (6), 1049–1051.—Carotenoids may be separated into three fractions—carotene hydrocarbons, monohydroxycarotenoids and polyhydroxycarotenoids—by partition chromatography of a light-petroleum soln. on silica gel pretreated with methanol, and successive elution with light petroleum, light petroleum - diethyl ether (1:1), and methanol. Results are described for the separation of the carotenoid pigments from Texas red grapefruit. The properties of the pigments are unchanged by the treatment and recovery is >90%. The mechanism of the separation is thought to be one of partition of the pigments between the mobile phase and methanol which is held as a stationary phase by the silica gel.

S. M. MARSH

4338. Analytical methods for differentiating the saponins. J. L. Fontán-Candela (Biochem. Lab., Fac. of Pharm., Madrid). *Bull. Soc. Chim. Biol.*, 1958, **40** (2–3), 503–510.—Two rapid methods of distinguishing between steroid and triterpenic saponins are examined. The characteristics of foams produced are investigated and the "total time," which is the life of the foam from production in an apparatus described until the liquid phase occupies nine-tenths of its original vol., is found to be characteristic of the type of saponin. Paper chromatography is also used. *Procedure*—Green-plant fragments (100 g) are shaken with water at 80° for 2 hr., the extract is treated with CCl_4, and 230-ml fractions of the remaining soln. are adjusted to pH 1 and pH 13, respectively. The "total time" of foaming is then determined for each fraction by passing air through a fine porous disc at 40 cm (Hg) pressure. If the "total time" at each pH is much the same, the saponin is triterpenic, but if that at pH 13 is several times as great as that at pH 1, it is steroidic. Chromatography is carried out on an aq. phase prepared as before and evaporated nearly to a syrup. Spots of extract are placed on Whatman No. 1 paper and the chromatogram is run for 24 hr. across the grain, with toluene as stationary phase and water - butanol - ethanol (1:1:1) as the mobile phase. The spots are revealed with $SbCl_3$, Sudan III and blood on separate chromatograms. Triterpenic saponins give a blue fluorescence with u.v. light with the $SbCl_3$ spots, and steroid saponins a yellow fluorescence.

E. J. H. BIRCH

4339. Polarographic determination of phosphorus, nitrates, potassium and calcium [in soil]. A. E. Petrov-Spiridonov. *Udobrenie i Urozhaĭ*, 1957, (11), 44–46; *Ref. Zhur., Khim.*, 1958, Abstr. No. 28,390.—An indirect polarographic determinatio

of P, based on the ability of PO_4^{3-} to form an insoluble ppt. with uranyl acetate in acid medium, is described. To 5 ml of soln. add 2 ml of 0·002 *M* uranyl acetate, warm to 70°, then cool to room temp., and to 1·5 ml of the supernatant soln. add 1·50 ml of 0·125 *M* Na acetate acidified to pH 4·8 to 5·5, and polarograph against the S.C.E. This gives the excess of uranyl acetate after the pptn. of PO_4^{3-}, the reduction potential being − 0·38 V. The concn. of P which may be determined is 0·5 to 10·5 mg per litre; the error is $< \pm 2\%$. No interference is caused by Cl^-, NO_3^-, SO_4^{2-}, Fe^{3+}, Zn^{2+}, Mn^{2+} or Co^{2+}, or by K^+, Ca^{2+} or Mg^{2+} if their concn. in the soln. is $< 0{\cdot}02$ *N*. To determine NO_3^- polarographically use 3 ml of 0·00066 *N* uranyl acetate in 0·1 *N* HCl, and 2 ml of soln. to be analysed and bubble CO_2 through the soln. for 4 min. The reduction potential of NO_3^- is −0·8 V. There is a linear relationship between concn. of NO_3^- and wave height for 0 to 10 mg of NO_3^- per litre. The error of the determination is $< 1\%$. No interference is caused by Cl^-, PO_4^{3-}, SO_4^{2-}, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, oxalates, tartrates or citrates, or by < 300 mg of carbohydrates and amino acids per litre. Polypeptides and albumins interfere in the determination of NO_3^-. The polarographic determination of K and Ca is made in the usual manner. By the methods described, P, NO_3^-, K and Ca can be determined directly on HCl extracts of some soils but soils rich in organic matter must first be purified by passing the extracts through ion-exchange resins. C. D. KOPKIN

4340. **A modified procedure for the fractionation and determination of soil phosphorus.** M. H. Bertheux (Univ. Coll. of Ghana, Achimota, Accra, Ghana). *J. Sci. Food Agric.*, 1958, **9** (3), 177–181.—Modifications are made to the Williams phosphorus fractionation method (*J. Agric. Sci.*, 1950, **40**, 233) to make it suitable for the rapid routine analysis of soils of low P content. The main modifications are (*i*) the use of a more rapid method for the treatment of the acetic acid and NaOH extracts before PO_4^{3-} determination, (*ii*) the reduction of amount of sample and extractant to enable a small centrifuge to be used, and (*iii*) the use of a higher extraction temp. Modifications are also made to Sherman's method for the determination of total P (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 182) in which the quantities are reduced to 1 g of sample digested with 6 to 8 ml of 60% $HClO_4$. H. B. HEATH

4341. **Cobalt determination in soils and rocks with 2-nitroso-1-naphthol.** L. J. Clark (Soil and Water Conserv. Res. Div., Dept. of Agric., Beltsville, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1153–1156.—Less than 10 μg of Co in the sample soln., prepared as described previously (*cf. Anal. Abstr.*, 1956, **3**, 1341), can be determined directly and accurately by extracting the 2-nitroso-1-naphthoxide complex into *iso*amyl acetate at 20°, and then measuring the extinction of the colour-stable extract at 530 mμ in a cell (75 mm × 12 mm), with *iso*amyl acetate as reference liquid. Interference by other metals is controlled (*i*) for Fe^{II} by oxidation with bromine water, (*ii*) for Sn^{II} by addition of bromine water and 10% aq. $Na_2S_2O_3$ soln., (*iii*) for Ni and Cu by successive shakings of the extract with *N* HCl and *N* NaOH, and (*iv*) for Mn and Pd by addition of 10% aq. $Na_2S_2O_3$ during the colorimetric procedure. The lower limit of sensitivity is 0·1 μg of Co in 10 ml of soln. W. J. BAKER

4342. **Application of ion exchange to flame spectrophotometry and determination of potassium in fertilisers.** C. W. Gehrke and E. L. Wood. *Missouri Univ. Agric. Exp. Sta. Res. Bull.*, No. 635, 1957, 60 pp.—The sample was dissolved in water and boiled with ammonium carbonate to precipitate Ca and Mg. The filtrate was adjusted to pH 5 with HNO_3, thereby liberating CO_2, and was shaken with Amberlite IR-4B (nitrate form) to remove phosphate. Alternatively, an ion-exchange column with an automatic device for elution with water was used. The resulting soln. containing 20 to 60 p.p.m. of K was analysed by flame spectrophotometry; KNO_3 was used for preparing standard curves. With the procedure recommended the small amount of Na present had little effect. The interfering action of added PO_4^{3-}, SO_4^{2-}, oxalate and NH_4Cl was also studied. Results compared satisfactorily with those of the A.O.A.C. gravimetric methods. NUTR. ABSTR. & REV.

4343. **Determination of 1-naphthylacetic acid by ultra-violet spectrophotometry.** Kaname Nomura (Yasugawa Plant., Sankyo Co.). *Ann. Rep. Takamine Lab.*, 1956, **8**, 242–246.—Methanolic soln. (containing 0·1 *N* H_2SO_4) of 1-naphthylacetic acid (**I**) give a max. absorption at 223 mμ, the extinction being proportional to concn. within the range of 0·02 to 0·1 mg per 50 ml. Aq. soln. of the sodium salt of **I** also give the same absorption curve with a slightly lower extinction coeff. No interference results from $NaHCO_3$, talc, starch, Na acetate and acetic acid. An aq. soln. of the sample (a commercial preparation) (0·01 to 0·1 mg per ml) (3 ml) is diluted with water (2 ml), 6 *N* H_2SO_4 (1 ml) and methanol to 50 ml. The results compare favourably with those by Rooney's volumetric method (*Anal. Chem.*, 1947, **19**, 475). The time taken for a determination is ≃30 min. K. SAITO

4344. **A detailed summative analysis of the crude fibre and nitrogen-free extractives fractions of roughages. I. Proposed scheme of analysis.** B. D. E. Gaillard (Lab. of Animal Physiol., Agric. Univ., Wageningen, Netherlands). *J. Sci. Food Agric.*, 1958, **9** (3), 170–177.—A system of analysis is described for the evaluation of feeds in which determinations of crude fibre and N-free extractives are replaced by determinations of the sugars of which the soluble and structural carbohydrates are composed, of pure cellulose and of lignin. The method is not recommended for routine analysis. H. B. HEATH

4345. **Determination of the lower fatty acids in silage by counter-current distribution.** D. Purves (Edinburgh and E. Scotland Coll. of Agric., 13 George Sq., Edinburgh, 8). *J. Sci. Food Agric.*, 1958, **9** (3), 137–140.—A method is described in which an aq. extract of silage is clarified by pptn. of $Cu(OH)_2$ in the liquid and an aliquot submitted to a 50-transfer counter-current distribution. The solvent system used is *iso*propyl ether - *M* phosphate buffer (pH 5·0). At the end of the run the contents of the tubes are steam-distilled and the volatile acid content is determined by titration. The acid content in the range C_2 to C_5 is calculated from values of partition ratios (*K*) previously determined with standard solutions. H. B. HEATH

4346. **Determination of the gamma-isomer content of hexachlorocyclohexane [BHC] dip-washes.** J. D. Mullen (African Explosives and Chemical Industries Ltd., Northrand, Transvaal, S. Africa). *Anal.*

Chim. Acta, 1958, **18** (3), 189–192.—The gamma isomer in a mixture of hexachloro*cyclo*hexanes is determined cryoscopically, pure gamma isomer being used as the cryoscopic solvent. When the sample contains substances other than hexachloro*cyclo*hexanes the effective mol. wt. is obtained by measuring the freezing point depression effect on benzene. Dip-wash samples are treated with a soln. of Na_2CrO_4 and H_2SO_4 to precipitate the hexachloro*cyclo*hexanes and to destroy many of the impurities. W. C. JOHNSON

4347. **Polarography of agricultural chemicals. VI. Determination of gamma-BHC mixed with parathion.** Shigeru Yamamoto and Kaname Nomura (Yasukawa Plant, Sankyo Co., Shiga-ken). *Ann. Rep. Takamine Lab.*, 1956, **8**, 219–226.—Although gamma-BHC (**I**) interferes in the polarographic analysis of parathion (**II**), the effect of **II** on the polarography of **I** is small. **I** (< 2 mg per 10 ml) is determined in 40% dioxan containing 10% of 0·2 *N* tetramethylammonium bromide and 0·01% gelatin at pH 10 ($E_{\frac{1}{2}}$ *vs.* the S.C.E. = − 1·03 V). The wave height increases linearly with increase in amount of **II**. **II** is determined by the diazotitration method and the wave height is corrected. The error for **I** is ≃ 2%.

VII. Polarographic determination of parathion mixed with gamma-BHC. Shigeru Yamamoto. *Ibid.*, 1956, **8**, 226–231.—In 40% ethanolic soln. of pH 6 containing 10% of 0·2 *N* NaCl, **II** exhibits a reduction wave of $E_{\frac{1}{2}}$ = − 0·69 V. In the presence of a large amount of **I** (> 3 mg per 10 ml), the wave height is greater; for the analysis of a commercial sample (*e.g.*, 0·5% of **II**, 2% of **I**), however, there is little interference. The working curve is linear for < 0·8 mg of **II** per 10 ml. The sample (0·1 g) is dissolved in ethanol (10 ml), and a 4-ml portion is mixed with 0·2 *N* NaCl (1 ml) and Kolthoff buffer (pH 6) (containing 0·01% gelatin) (5 ml) and polarographed after passage of H. The coeff. of variation is ≃ 1·3%. K. SAITO

4348. **Determination of residues of OO-diethyl S-*iso*propylcarbamylmethyl phosphorodithioate in olive oil and in fruits.** B. Bazzi (Ist. Ricerche Agr., Firenze). Publ.: Soc. Gen. per l'Ind. Min. e Chim., Milano, 1957, 16 pp.—A micro-method is described for the colorimetric determination of this insecticide; it involves extraction of the active substance with appropriate solvents from the oil or fruit and subsequent isolation from interfering compounds of P by micro-distillation under controlled conditions according to Otter [*Mikrochim. Acta*, 1956, (1–3), 125], followed by the colorimetric determination of P. It has been established that the distillation does not cause any modification of the insecticide. As little as 0·2 p.p.m. can be determined in olive oil and 0·1 p.p.m. in apples or peaches. P. HAAS

4349. **Determination of endrin in agricultural products and animal tissues.** J. M. Bann, S. C. Lau, J. C. Potter, H. W. Johnson, jun., A. E. O'Donnell and F. T. Weiss (Shell Development Co., Agric. Res. Div., Modesto, Calif.). *J. Agric. Food Chem.*, 1958, **6** (3), 196–202.—The procedure described was developed to replace bio-assays by a chemical procedure more specific than combustion - chlorine methods. It involves extraction with hexane and *iso*propyl alcohol (or acetone for soils), hydrolysis of fat if present, separating endrin on a column of Florisil and magnesia - Celite, eluting with hexane, heating with sodium in *iso*propyl alcohol and methanol, and treating the hexahydro- and octahydro-methanonaphthalenes that are formed with phenyl azide to give phenyldihydrotriazoles. These triazoles react with diazotised sulphanilic acid in acid medium to give an intense red pigment, with max. absorbance at 515 mμ. As little as 5 μg of endrin can be measured. Other chlorinated insecticides interfere if the chromatographic step is omitted, but with it only chlordane and dieldrin interfere significantly. To obtain the most reliable figures, the endrin value for a sample should be corrected for the apparent endrin value for an insecticide-free control sample analysed concurrently. M. D. ANDERSON

4350. **Determination of 2:3-*p*-dioxandithiol SS-bis-(OO-diethyl phosphorodithioate) [Delnav] [Hercules AC-528].** C. L. Dunn (Res. Centre, Hercules Powder Co., Wilmington, Del.). *J. Agric. Food Chem.*, 1958, **6** (3), 203–209.—This new pesticide is determined by extraction of the sample with hexane or hexane - *iso*propyl alcohol, chromatography on acid alumina and then on Celite, cleavage of the C–S bond in the eluted Delnav with $HgCl_2$, and conversion of the resulting glyoxal into the 2:4-dinitrophenylosazone, which is measured gravimetrically or colorimetrically. For oils and fats, preliminary partitioning between solvents such as methyl cyanide and benzene is required before chromatography. A compact apparatus is described for simplifying and hastening chromatographic procedures. M. D. ANDERSON

4351. **Persistence of residues of 2:3-*p*-dioxandithiol SS-bis-(OO-diethyl phosphorodithioate) [Delnav] [Hercules AC-528] as an acaricide on and in mature lemons and oranges.** F. A. Gunther, L. R. Jeppson, J. H. Barkley, L. M. Elliott, R. C. Blinn and C. L. Dunn (Univ. of Calif. Citrus Exp. Sta., Riverside). *J. Agric. Food Chem.*, 1958, **6** (3), 210–211.—Residues of this acaricide on sprayed citrus fruits were determined by the method described previously (*cf.* Dunn, *Anal. Abstr.*, 1958, **5**, 4350). The half-life was about 95 and 85 days on orange and lemon peel, respectively. Less than 0·03 p.p.m. was found in the edible portion of the fruits. In drying citrus peel for cattle food, 60% of the original residue remained. M. D. ANDERSON

4352. **Determination of *m*-dinitrophenyl pesticides.** C. Menzie (Bureau of Sport Fisheries and Wildlife, U.S. Fish and Wildlife Service, Laurel, Maryland). *J. Agric. Food Chem.*, 1958, **6** (3), 212–213.—As little as 2 μg of a *m*-dinitrophenyl pesticide can be simply and rapidly determined by heating with KCN to give a coloured product, measured at 350 mμ. The reaction could also be used to determine DDT, methoxychlor, or BHC, after nitration. M. D. ANDERSON

See also Abstracts—**4105**, Determination of F^- in agricultural chemicals. **4180**, **4181**, Determination of organic acids. **4183**, Determination of malic acid. **4232**, Determination of tartronate in tissues.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

4353. **Magnetically operated needle valve.** J. O. Cope (Chem. Phys. Sect., Div. of Ind. Chem., C.S.I.R.O., Melbourne, Australia). *Rev. Sci. Instrum.*, 1958, **29** (3), 232–234.—Details are given of solenoid-operated needle valves (glass and metal) which have a cut-off valve of approx. 10^{-4} micron-litre per sec. The valve seat is made from polytetrafluoroethylene and sticking is minimised by superimposing a 50 c.p.s. voltage on the solenoid. Smooth and rapid control of gas-flow rates over a wide range is achieved. G. SKIRROW

4354. **Anomalous copper results with the use of porcelain crucibles.** H. Zeitlin, M. M. Frodyma and G. Ikeda (Dept. of Chem., Univ. of Hawaii, Honolulu). *Anal. Chem.*, 1958, **30** (7), 1284–1286.—Porcelain crucibles commonly available in the U.S.A. are apparently made from materials which contain appreciable amounts of Cu. Ignition with an alkaline flux at 700° to 800° is sufficient to extract the Cu from the porcelain surface.
G. S. ROBERTS

4355. **Automatic titrator.** L. Gavanda. *Mitt. Chem. ForschInst. Wirtsch. Öst.*, 1957, **11** (3), 77–78.—A fully automatic titrator which is operated by pH control is described and illustrated. It comprises the titrator proper, which regulates the feed of the titrating fluid by means of electromagnetically operated cocks, coupled with a pH meter and its pertaining electrode circuit. The pH meter governs the titration according to the difference in potential against the electrode system which dips into the fluid to be titrated. Provision is made for manual operation over part of the titration. The apparatus may also be used for conductivity measurements and responds to monitoring by colorimetric and absorptiometric instruments. The instrument is exact to ± 1 drop provided that the deflection at the end-point remains stable within 0·1 pH unit or 10 mV, and adapts itself to the reaction speed of the titrating operation.
C. A. CURTIS

4356. **Compact counter-current distribution apparatus.** S. Raymond (Coll. of Physicians and Surgeons, Columbia Univ., New York). *Anal. Chem.*, 1958, **30** (7), 1214–1216.—An automatic apparatus is described in which compactness is a special feature, a 24-in. square base being sufficient to house a 100-tube unit together with automatic drive mechanism. The apparatus has been used successfully in several laboratories, but has been criticised on the grounds that only 20 of the 100 tubes are fully visible. G. S. ROBERTS

4357. **Dialysis as an analytical tool.** H. Hoch and R. C. Williams (Dept. of Biophysics, Med. Coll. of Virginia, Richmond, U.S.A.). *Anal. Chem.*, 1958, **30** (7), 1258–1262.—A simple apparatus and technique are described for measuring dialysis rates in order to detect differences in mol. size and to establish another test for heterogeneity.
G. S. ROBERTS

4358. **Technical improvement of two-dimensional paper chromatography.** U. Vetsch and H. Lüthi (Versuchsanst. für Obst-, Wein- und Gartenbau, Wädenswil, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1958, **49** (1), 29–35.—In this modification of two-dimensional chromatography, three parallel runs of the sample soln., with reference substances, are made on the same sheet of suitably buffered paper (30 cm × 50 cm). The spots are revealed on one strip to show the position of the separated components, then one of the other strips is cut off and sewn to another sheet of paper for the second-dimensional run at 90° to the first. For application to the separation of amino acids in fruit juices and wine, the paper used was buffered at pH 9·3, the first solvent was butanol - acetic acid - water (4 : 1 : 1), and the second was phenol - *m*-cresol (1 : 1) (*cf.* Levy and Chung, *Anal. Chem.*, 1953, **25**, 396). Advantages of the method are discussed.
S. BAAR

4359. **Automatic recording apparatus for use in the chromatography of amino acids.** D. H. Spackman, W. H. Stein and S. Moore (Rockefeller Inst. for Med. Res., New York). *Anal. Chem.*, 1958, **30** (7), 1190–1206.—A recording instrument is described which, in conjunction with improvements in ion-exchange chromatography, enables the complete quant. determination of amino acids in a hydrolysate of a peptide or a protein to be made in 24 hr. Ninhydrin reagent is introduced at a constant rate into the eluate flowing from the column. Colour development occurs as the mixture is pumped through a coil heated to 100° and the intensity of the blue colour is determined by continuous photometry at 570 mμ. The yellow colours from proline and hydroxyproline are also monitored at 440 mμ. The peaks on the recorded curves can be integrated with a precision of 100 ± 3% at levels of 0·1 to 3 μmoles of each amino acid; useful results can be obtained at the 0·06-μmole level owing to the stability of the base line. More complex mixtures characteristic of biological materials can be analysed in two days. Comprehensive data and diagrams of the instrument are illustrated.
G. P. COOK

4360. **Description of a densitometer for direct colorimetry of irregularly shaped chromatographic spots.** R. J. Wieme (Lab. of the Med. Clinic, Univ. of Ghent, Belgium). *J. Chromatography*, 1958, **1** (2), 166–171.—An apparatus is described in which a moving spot of light (2 mm × 2 mm) is obtained by rotating a slit of 2-mm width in front of a slightly curved stationary slit (2 mm × 25 mm), the chromatogram, rendered translucent by oiling, being moved in 2-mm steps between the stationary slit and a photocell. At each step the material along the stationary slit is scanned by the moving spot, giving a galvanometer reading which, plotted on linear graph paper, yields a curve, the area under which is a measure of the total amount of material in the chromatographic spot. For the galvanometer deflection to be directly proportional to the amount of material distributed along the stationary slit, the log. of the amount of light absorbed, not the amount itself, must be integrated, and the photomultiplier circuit described allows for this. Tests with Amido black showed a coeff. of variation of about 2%, and comparative analyses of human serum showed good agreement between results by the densitometer and by elution followed by conventional colorimetry. The apparatus can be used to scan a magnified coloured image, and may be useful in histochemistry. R. E. ESSERY

4361. **A modified technique in chromatography.** K. Krishnamurti and B. V. Dhareshwar (Coll. of Sci., Nagpur, India). *Nature*, 1958, **181**, 766–767.—Sharp separations of inorganic ions can be produced by the use of strips of filter-paper impregnated with an agar soln. containing reagents with which the radicals to be separated will react. It is claimed that the solubility of sparingly sol. substances can be deduced from these chromatograms, by measuring the distance travelled by the front of the band and by using an empirical equation.

G. S. ROBERTS

4362. **Apparatus for preparation of banded paper chromatograms.** J. H. Reinhart, J. W. Brown and R. L. Weintraub (Chem. Corps Biol. Lab., Fort Detrick, Md., U.S.A.). *Chemist Analyst*, 1958, **47** (1), 18.—An apparatus is described which facilitates the uniform application of bands of material on paper. The paper is held on an aluminium drum of suitable circumference (13·5 in.) geared to a suitable speed of rotation (2 to 8 r.p.m.), so that the solvent evaporates from the paper during a single revolution. The solutions are applied from open hypodermic syringes, supported so that they can swivel freely, with the needle-tips in continuous contact with the paper under light pressure. Appropriate needle gauges and drum speeds are determined for each solvent, and evaporation can be hastened by fan or lamp. The volume of solvent which can be applied is unlimited, but is governed in practice by the solute content and the particular paper being treated. Application of pressure to the feed, except to open blocked needles, is not beneficial. Solutions in water, ethanol and ether have been banded successfully.

R. E. ESSERY

4363. **Programmed-temperature gas chromatography.** S. Dal Nogare and C. E. Bennett (E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1157–1158.—By linearly increasing the column temp. during gas chromatography and maintaining a constant-vol. gas flow, each solute is eluted at a characteristic vol. and temp. Mixtures with wide boiling-point ranges can be separated rapidly by varying the column temp. over a wide range. All the solutes, even with a boiling-range as wide as 200°, emerge as well-defined peaks of nearly the same shape.

K. A. PROCTOR

4364. **Flame-ionisation detector for gas chromatography.** I. G. McWilliam and R. A. Dewar (I.C.I. Australia and New Zealand Ltd., Central Res. Lab., Ascot Vale, Victoria, Australia). *Nature*, 1958, **181**, 760.—The electrical conductivity of a hydrogen - nitrogen flame is very sensitive to traces of organic vapour. A detector was constructed based on this principle and comprising a hypodermic needle, which served as gas jet and positive pole, and a brass gauze set 1 cm above the needle tip. A deflection of twice background was produced by 4×10^{-10} g of diethyl ether in ethyl acetate. The sensitivity at the point of detection was about 1 part in 400 million (by vol.). The apparatus has been found to be little affected by carrier gas (N + H) composition, vibrations, flow rate, etc.

G. S. ROBERTS

4365. **Note on gas radiochromatography.** G. Moussebois and G. Duyckaerts (Lab. de Chim. Anal., Univ. de Liége, Belgium). *J. Chromatography*, 1958, **1** (2), 200–201 (in French).—A simple gas-chromatography apparatus, suitable for the analysis of mixtures of alkyl iodides labelled with ^{134}I, is illustrated. The measurement is made by passing the exit gases from the column through a small Dewar flask, placed in the cuvette of a γ-scintillator which is connected to a ratemeter, superscaler and recorder. Results are given for the resolution of a mixture of labelled ethyl, *n*-propyl, *iso*propyl, *n*-butyl and *iso*butyl iodides, a column of fire-brick (48 to 60 mesh) (120 cm × 0·5 cm) being used, with dinonyl phthalate as stationary phase and N as carrier gas (16 ml per min.), at 100°. The combination of radioactive with ordinary thermal detection enables specific activity to be determined, by comparison of the two records.

R. E. ESSERY

4366. **High-temperature viscometer.** Z. Menčík (Res. Inst. Macromol. Chem., Brno, Czechoslovakia). *Chem. Průmysl*, 1958, **8** (1), 24–25.—A viscometer of the Ubbelohde type is described which is suitable for measurements of polymer soln. at temp. up to ≃ 160°. The apparatus enables work to be done in air as well as in an inert atmosphere. The advantage of the apparatus is that all operations connected with the measurement (cleaning, filtration, rinsing) are carried out in the bath at elevated temp. The kinetic energy correction has been minimised by employing two horizontal capillaries.

J. ZÝKA

4367. **Mechanical smoking device[s] specially designed for the determination of carcinogenic substances in tobacco smoke.** A. Dobrowsky (Chem. Forschungsinst. der Wirtschaft Österreichs, Lothringerstrasse, 16, Wien III, Austria). *Mitt. chem. ForschInst. Wirtsch., Öst.*, 1958, **12** (2), 33–42.—Two devices are described by which intermittent suction of 40 ml of smoke during 2 sec. is achieved, in one case by means of the regulated fall in a column of water, and in the other by the movements of a piston in a glass tube. The chief improvement on previous designs comprises the maintenance of a reasonably constant reduction of pressure throughout the period of suction. Regulating mechanisms for the control of the intake of smoke and its discharge into cotton wool are included in the designs. An aperiodic manometer for use with these devices is described.

P. S. ARUP

See also Abstracts—**4252**, Reactor - gas chromatography for amino acids. **4253**, Automatic equipment for determination of amino acids.

Optical

4368. **Agar as specimen carrier in double-beam infra-red spectroscopy.** J. G. Feinberg, H. D. C. Rapson and M. P. Taylor (Beecham Res. Lab., Betchworth, Surrey, England). *Nature*, 1958, **181**, 763–764.—Dissolved or suspended substances, *e.g.*, pollen polysaccharides, may be prepared for i.r. spectroscopy by incorporating them in an agar film. A 0·8% stock soln. is made from purified commercial agar. The material for examination is suspended in water and then mixed with an equal vol. of agar stock at ≃ 56°. A small vol. (2 ml) of the warm mixture is pipetted on to a silicone-treated glass plate and confined to a definite area by a metal or plastics ring (1·5 in.). A control film is prepared at the same time. When the films have

set, the rings are removed and the discs are air-dried at 37°. The dried films can be manipulated with ease. G. S. ROBERTS

4369. **Use of substitute standards in infra-red differential spectrophotometry.** W. H. Washburn and M. J. Mahoney (Abbott Lab., North Chicago, Ill., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1053–1055.—The interference caused by impurities in the reference standard in the i.r. differential analysis of a compound for a specific impurity can be overcome to a great extent by substituting for the reference standard a pure compound of different chemical structure but with nearly identical absorption characteristics in the wavelength region being used. The important factors in selecting such a substitute are discussed. K. A. PROCTOR

4370. **Small-volume five-centimetre absorption cell.** G. Goldberg, A. S. Meyer, jun., and J. C. White (Oak Ridge National Lab., Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1163–1164.—The cell described has a capacity of about 4 ml and can be used with the Beckman model DU and B spectrophotometers. It is easily filled, drained and cleaned, and is inert to various solvents and acids. The max. absorbance difference between a set of such cells filled with acetone over the range 300 to 500 mμ was 0·010. K. A. PROCTOR

4371. **Variable path-length absorption cells for liquids.** General Instruments Co., Ltd., and J. Tadayon. Brit. Pat. 796,745; date appl. 30.1.56.—The cell comprises a slidable but non-rotatable inner member mounted within an outer member. Each member has an aperture and means for securing a window to close the aperture so that the opposing inner surfaces of the windows are parallel to one another and perpendicular to the relative movement of the members. An adjusting device, comprising a screwed collar, enables the path-length to be varied. J. M. JACOBS

4372. **Optical arrangement for comparing the transmission ratio of a sample with a standard.** Carl Zeiss Stiftung. Brit. Pat. 796,661; date appl. 1.6.56. Germany, date appl. 2.6.55.—In comparative objective photometry, *e.g.*, in the colorimetric determination of the concn. of soln., two pencils of rays, one passing through the specimen to be measured and the other through the reference substance, are compared for their intensity. An optical arrangement is described comprising an interference polariser for splitting the pencil of rays into a measuring beam and a comparison beam, and for re-combining the beams, together with an optical element suitable for determining the degree of polarisation (by direct measurement or zero balancing) for analysing the re-combined beam. J. M. JACOBS

4373. **Evaluating concentrations of spectrally absorbing vapours in dynamic systems. Spectrophotometric techniques and equipment.** F. A. Gunther, R. C. Blinn, M. J. Kolbezen, C. W. Wilson and R. A. Conkin (Univ. of California, Citrus Exp. Sta., Riverside, U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1089–1095.—The techniques described for determining trace amounts of NH_3 in air are based on the use of both a manually operated spectrophotometer and an automatic multi-sampling apparatus incorporating a ratio-recording spectrophotometer. The methods are applicable to fumigants or vapours which absorb selectively in the u.v. region. K. A. PROCTOR

4374. **Use of perchloryl fluoride in flame photometry.** G. E. Schmauch and E. J. Serfass (Chem. Dept., Lehigh Univ., Bethlehem, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1160–1161.—Perchloryl fluoride (ClO_3F) is a colourless, non-corrosive gas which can be stored as a liquid under pressure. It exhibits oxidising properties and, in combination with 2 to 3 vol. of H, produces an easily controlled, bluish flame in a modified Beckman burner, with sufficiently low background for use as an excitation source in flame photometry. K. A. PROCTOR

4375. **The Rouy method for photo-electric polarimetry.** B. Carroll, H. B. Tillem and E. S. Freeman (Chem. Dept., Rutgers, State Univ., Newark, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1099–1101.—A photo-electric colorimeter can be converted into a highly sensitive polarimeter by means of a set of adapters, each with two Polaroid plates. The theory, apparatus and experimental data of the conversion are considered. Reproducible rotations of ± 0·001° have been obtained. K. A. PROCTOR

4376. **Alarms and analysers for nerve-gas vapours.** R. H. Cherry, G. M. Foley, C. O. Badgett, R. D. Eanes and H. R. Smith (Leeds & Northrup Co., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (7), 1239–1247.—Three types of instrument are described for the detection of nerve gas in air. One is a precision analytical tool, another a rugged, portable apparatus suitable for use outdoors, and the third is an alarm intended for use in production plants and storage areas. All three depend on the optical determination of the fluorescent compound indoxyl, produced by the oxidation of a buffered alkaline soln. of indole by acid-stabilised H_2O_2 in the presence of nerve gas (Schoenemann reaction). Although this oxidation proceeds slowly when only the reagents are present it is greatly accelerated by traces of nerve gas which, at concn. of the order of 1 μg per litre of air, produces quantities of fluorescent material proportional to the nerve gas concn. All three instruments may be used as alarms to give warning of nerve-gas concn. below the lethal level. G. S. ROBERTS

4377. **Portable, automatic alarm for detection of toxic agents in atmosphere.** J. C. Young, J. R. Parsons and H. E. Reeber (Chem. Warfare Lab., Army Chem. Center, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (7), 1236–1239.—A robust, portable instrument has been developed for the detection of nerve gases (alkyl fluorophosphates) at concn. as low as 0·02 p.p.m. The atmosphere is sampled by a pump which passes the air through a paper filter to remove dust, and then through an α-cellulose tape which is wetted with a soln. containing *o*-dianisidine and sodium peroxypyrophosphate at pH 9. Nerve gas present in the air sample is oxidised by the peroxide and the oxidation products react with *o*-dianisidine producing a red coloration. Sections of the wetted tape before and after treatment with the air sample are scanned by a balanced system of photocells. A 30% change in the total amount of reflected light from the surface of the tape unbalances the electronic circuit and operates an alarm. Several volatile substances used in wartime were tested for chemical interference. These included by-products from the detonation of high

explosive and incendiary bombs and coloured smokes. Of these substances only N_2O_4, Cl and chlorosulphonic acid smoke caused interference.

G. S. ROBERTS

Thermal

4378. **High-temperature thermal-conductivity cell.** H. R. Felton and A. A. Buehler (E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1958, **30** (6), 1163.—Model aeroplane "glow plugs" are used as the sensing elements in this cell, which is said to give satisfactory performance even above 400°. K. A. PROCTOR

4379. **The derivatograph. I. An automatically recording apparatus for the simultaneous plotting of thermogravimetric, differential thermogravimetric and derivative thermogravimetric curves.** F. Paulik, J. Paulik and L. Erdey (Inst. für Allgemeine Chemie der Tech. Univ., Budapest). *Z. anal. Chem.*, 1958, **160** (4), 241–252.—The apparatus is described in detail and some examples of its use are given (*cf. Anal. Abstr.*, 1957, **4**, 767).

II. Gravimetric micro-distillation method for the study of liquids. F. Paulik, J. Paulik and L. Erdey. *Ibid.*, 1958, **160** (5), 321–324.—A micro-distillation apparatus is described which, fitted to a thermobalance, enables the weight distilled, the rate of distillation and the equilibrium temperatures to be simultaneously recorded. The derivative recording apparatus is described in Part I. From the curves obtained, the composition of $< 0{\cdot}5$ g of a mixture of liquids can be determined. The analysis of a mixture of benzene, ethanol and water in the ratio 39·0:50·7:10·3 with the result 36·5:52·9:10·6 is given as an example. A. R. ROGERS
G. BURGER

Electrical

4380. **A micro-electrophoretic method.** J. Kohn (Path. Dept., Queen Mary's Hosp., Roehampton, London). *Nature*, 1958, **181**, 839.—A micro modification of an earlier method (*cf. Anal. Abstr.*, 1958, **5**, 1747) is described. Cellulose acetate strips (10 to 12 cm × 2·5 cm) are used. A clear separation of all protein fractions is obtained with 0·1 to 8 μl of serum. The strips are stained in 0·005% Nigrosin soln. in 2% acetic acid for 1 hr. One post- and two pre-albumin fractions can be seen. The method is suitable for combination with immunoelectrophoresis. S. BAAR

4381. **Portable apparatus for paper electrophoresis.** G. B. Marini-Bettolo and J. A. Coch Frugoni (Lab. of Therapeut. Chem., Ist. Super. di Sanità, Rome). *J. Chromatography*, 1958, **1** (2), 182–185.—A portable apparatus for use in the field is described and illustrated. The application of the equipment to the examination of *Strychnos* barks for alkaloids is described; an analysis takes 1 hr. For clinical diagnostic or other purposes, when electric current is available, the dry battery normally present can be replaced by a rectifier.
R. E. ESSERY

4382. **Recording densitometer with a photoelectric multiplier.** L. P. Shuvatov. *Lab. Delo*, 1957, **3** (6), 39–41.—An apparatus for recording the density of electrophoresis spots, especially of blood-protein fractions, consists of a paper-rotating mechanism, a photo-electric multiplier, an a.c. amplifier and a pen-recording device. E. HAYES

4383. **Densitometer for the measurement of electrophoresis spots.** B. R. Kirichinskiĭ and B. A. Roĭtrub. *Lab. Delo*, 1957, **3** (5), 51–53.—A ray of light from a 12-V, 50-W lamp is projected through a condenser on to an electrophoresis spot, arranged so that it can be moved transversely, and the reflected light falls on a selenium photocell placed as near as possible to the paper. The current is measured directly on a galvanometer with a sensitivity of 10^{-7} to 10^{-8} amp. per mm. E. HAYES

4384. **Rotating hanging-mercury-drop electrode.** E. Barendrecht (Central Lab., Dutch State Mines, Geleen). *Nature*, 1958, **181**, 764–765.—This electrode system possesses several advantages over the conventional dropping-mercury electrode, and over the stationary hanging-drop electrode, namely, the charging current is reduced, the current - voltage curve can be scanned in a shorter time, and various sources of curve distortion are eliminated.
G. S. ROBERTS

4385. **Polarography of metal ions in fused lithium chloride - potassium chloride eutectic.** H. A. Laitinen, C. H. Liu and W. S. Ferguson (Dept. of Chem. and Chem. Engng, Univ. of Illinois, Urbana, U.S.A.). *Anal. Chem.*, 1958, **30** (7), 1266–1270.—The characteristics of the chlorides of Cd, Bi, Cr, Cu, Zn, Tl, In, Pb, Sn, Ga, Hg and Al have been studied in the fused eutectic at 450° with micro-electrodes of platinum, tungsten or carbon and a platinum reference electrode. Under suitable conditions, voltammetric measurements can be used for analytical purposes. K. A. PROCTOR

4386. **Automatic continuous coulometric titrimeter. I. Design and construction of a coulometric titrimeter.** Takeo Takahashi, Eiji Niki and Hiroshi Sakurai (Inst. of Ind. Sci., Yayoi-cho, Chiba). *Japan Analyst*, 1958, **7** (2), 93–98.—An automatic continuous titrimeter for a reducible component was designed, which involves the measurement of the electrolytic current necessary for producing Br (from H_2SO_4 soln. of KBr) equiv. to the component to be measured. The p.d. between the indicator electrodes is converted into an a.c. current, which is amplified, rectified and fed back to control the d.c. current for electrolysis. The relationship between the amount of the reducible component in the sample and the excess of Br in the reaction vessel is discussed and an electronic circuit proposed.

II. Working conditions of the coulometric titrimeter. Takeo Takahashi, Eiji Niki and Hiroshi Sakurai. *Ibid.*, 1958, **7** (2), 98–103.—The working conditions for the titrimeter, including the applied voltage, the rate of flow of the sample soln., the shape of the reaction vessel and the surface state of the indicator electrodes, are discussed. The transient state was examined with As_2O_3 soln.; the proportionality between the concn. of As_2O_3 and the electrolytic current is better when the applied voltage is close to the equilibrium voltage. Although the proportionality is improved by decrease in rate of flow, the stability of recording deteriorates. K. SAITO

4387. **Two-dimensional pulse-height analyser.** M. Birk, T. H. Braid and R. W. Detenbeck (Palmer Phys. Lab., Princeton Univ., N.J., U.S.A.). *Rev. Sci. Instrum.*, 1958, **29** (3), 203–209.—Circuit details are given for an analyser which classifies a coincident event between two detectors according to both pulse amplitudes. The events are sorted into channels covering a plane instead of the normal linear array. Examples are given of its application to a (p, $p'\gamma$) experiment and to the identification of the energetic charged particles by measuring simultaneously their energy and differential energy loss. G. SKIRROW

4388. **Permselective membrane electrodes. Analytical applications.** J. S. Parsons (American Cyanamid Co., Bound Brook, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (7), 1262–1265.—Cation- and anion-selective membranes have been made by moulding ion-exchange resins with a plastics binder. Cation permeability is provided by the sulphonated-type resins and anion permeability by quaternary amine resins. Although electrodes made of these membranes show an almost theoretical response over a limited concn. range to ions of a single species without interference from ions of opposite charge, the selectivity within ionic species is poor. The sodium form of a sulphonated polystyrene membrane has been used as a pNa electrode and other membranes have been used as indicator electrodes in the potentiometric titration of sulphate with barium acetate. Good end-points were obtained only in the absence of many other cations and anions. K. A. PROCTOR

4389. **Automatic titrator based on constant-current potentiometric titrations.** I. Shain and C. O. Huber (Chem. Dept., Univ. of Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1958, **30** (7), 1286–1288.—Titrations of Fe^{2+}, Mn^{2+}, $S_2O_3^{2-}$ and Cl^- have been made with the simple and inexpensive apparatus described. The results agreed well with those obtained by manual titration. The applicability of the instrument is confined to systems that produce some sort of peaked titration curve. K. A. PROCTOR

4390. **New applications of high-frequency measurements in analytical chemistry.** F. Oehme (Inst. Microbiol. and Exp. Therapy, Jena). *Chemie, Prague*, 1957, **9** (3), 366–378.—A survey of recent developments in high-frequency techniques. J. ZÝKA

4391. **Amperometric titration. (The positive electrode and its application to bromimetry.) VII. The use of a non-polarisable electrode of high positive potential.** Masayoshi Ishibashi, Taitiro Fujinaga and Chikayo Saito (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (1), 12–14.—Several positive-potential electrodes (*e.g.*, PbO_2 - Pb^{2+}, MnO_2 - Mn^{2+}, Ce^{4+} - Ce^{3+} and MnO_4^- - Mn^{2+}) were examined for use in short-circuit amperometry. Whilst Ce^{4+}, MnO_2, PbO_2 and BrO_3^- electrodes behave as non-polarisable electrodes and give results in good agreement with the theoretical, MnO_4^-, $Cr_2O_7^{2-}$ and VO_3^- electrodes are polarisable and their potentials are lower than expected. To obtain a positive potential, + 1·0 V *vs.* the S.C.E., MnO_2 (Mn^{2+}, 1 M; H^+, 1 M) and PbO_2 (Pb^{2+}, 1 M; H^+, $10^{-2\cdot3}$ M) are recommended.

VIII. Determination of arsenite with bromate by the use of a lead dioxide electrode. Masayoshi Ishibashi, Taitiro Fujinaga and Chikayo Saito. *Ibid.*, 1958, **79** (1), 14–16.—Since AsO_3^{3-}, AsO_4^{3-} and KBr do not give a polarographic wave at $<$ + 0·8 V *vs.* the S.C.E., the reduction wave due to BrO_3^- can be used for the titration of AsO_3^{3-} with $KBrO_3$. The sample soln. (0·05 to 50 mg of AsO_3^{3-}) in 3 N HCl is connected with the PbO_2 electrode (pH of the Pb^{2+} soln., 6·5) and titrated amperometrically with 0·002 to 0·2 N $KBrO_3$ at + 0·65 V. The error is $< 3\%$ and the titration compares favourably with that by the use of methyl orange indicator. K. SAITO

4392. **Advances in amperometric titration.** O. A. Songina. *Zavod. Lab.*, 1958, **24** (2), 160–166.—A review of papers published mainly in 1955 and 1956, with 93 references. G. S. SMITH

4393. **Improvement of a high-frequency titrimeter.** Kunio Nakano and Setsuko Shibata (Fac. of Sci., St. Paul Univ., Ikebukuro, Toshima-ku, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (1), 88–91.—The shielding of both condenser- and coil-type high-frequency titrimeters (*cf.* Nakano, *Anal. Abstr.*, 1956, **3**, 2388) can be achieved by the use of a modified apparatus without the aid of a conc. electrolytic soln. The container (diameter 3 cm) is covered with two bands of silver foil connected together with a fixed resistance. The peak of the fundamental curve (*cf.* Nakano, *Anal. Abstr.*, 1955, **2**, 1730, 1731; 1957, **4**, 777) becomes less distinct with decreasing resistance and increasing width of the metal bands. The appearance of a "pseudo" end-point due to the peak is thus eliminated. K. SAITO

4394. **A high-frequency titrimeter useful for a wide range of concentration.** Kunio Nakano, Hiroshi Tadano and Yoshiaki Ohira (Fac. of Sci., St. Paul Univ., Ikebukuro, Toshima-ku, Tokyo). *Japan Analyst*, 1958, **7** (2), 79–84.—For obtaining a monotonic fundamental curve, a combination of a condenser-type titrating vessel which is partly shielded electrostatically (Nakano, *Anal. Abstr.*, 1956, **3**, 2388) and a coil-type vessel with auxiliary electrodes (*Anal. Abstr.*, 1957, **4**, 777) is recommended. The outside wall of a double-walled glass cylinder (sample container) is wrapped with two bands of aluminium foil and a coupled platinum electrode is attached above the aluminium band. A dil. ($\simeq$ 0·001 M) NaCl soln. is placed between the two walls of the cylinder and both the aluminium and the platinum electrode pair are coupled electromagnetically with the oscillator (1 megacycle). By adjusting the electronic elements, a monotonic fundamental curve is obtained and an accurate titration can be made in the range 0·0007 to 5 M, both in neutralisation and pptn. titration. K. SAITO

4395. **High-frequency apparatus for physico-chemical studies and its applications.** V. A. Zarinskiĭ and I. R. Mandel'berg (V. I. Vernadskiĭ Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR). *Zavod. Lab.*, 1958, **24** (2), 148–153.—An apparatus giving high sensitivity and accuracy for high-frequency titrations under works and field conditions has been designed. Details are given, together with examples of its use. G. S. SMITH

4396. **Silver and thallium oxide coulometer.** W. T. Foley (Chem. Dept., St. Francis Xavier Univ., Antigonish, Nova Scotia, Canada). *J. Electrochem. Soc., New York*, 1957, **104**, 638–639.—A simple coulometer is described in which a soln. of Ag and Tl^{I} salts at pH 9·5 is used. The reaction proceeds according to the equation—

$$4Ag^{+} + 2Tl^{+} + 6OH^{-} = Tl_2O_3 + 3H_2O + 4Ag.$$

The electrolyte comprises 4 g of Tl_2SO_4, 4 g of $AgNO_3$, 4 g of NH_4NO_3 and 8 ml of 15 *M* aq. NH_3 in 300 ml of H_2O for a platinum-gauze cathode of $\simeq$40 sq. cm and an anode of $\simeq$23 sq. cm. For currents over the range 0·01 to 1 amp. and amounts of Ag 0·1 to 1 g, the amount of Ag deposited does not differ by more than $\pm$0·08% from the theoretical value. J. H. WATON

4397. **Current integration with permanent magnet d.c. motors in controlled potential coulometric analysis.** J. J. Lingane (Dept. of Chem., Harvard Univ., Cambridge, Mass., U.S.A.). *Anal. Chim. Acta*, 1958, **18** (4), 349–352.—The rotational speed of a permanent magnet d.c. motor is approx. linearly proportional to the energising voltage over a wide range, and when driving a revolution counter can be used to integrate time - voltage functions. An apparatus is illustrated which works accurately down to one-tenth of the nominal maximum voltage (*i.e.*, over a 10:1 range), below which the counting rate falls below the value required by strict linearity. The decay $\propto 1/iR$, where iR is the input voltage, and an equation is derived relating counting rate N to iR, which is correct to $\pm$0·3% over a 100:1 range of input voltage, and is in error by only $-$1·3% at one two-hundredth of the max. voltage. From this an equation is derived, relating the coulombs of electricity Q with N, of the form $Q = (N + \alpha t)/\beta R$, where t is the time occupied by the experiment and R is the shunt resistance. For controlled potential coulometric analysis, R should be selected so that iR is near the max. permissible at the start of the electrolysis. The current decays to a small background value, usually between 1/100 and 1/500. Under these conditions, the instrument can evaluate Q with an error $\not> -0{\cdot}3\%$.
R. E. ESSERY

4398. **Paper electrometry.** J. Žirnauskas (Litauischen Veterinärakad., Kaunas, Lithuania). *Chem. Tech., Berlin*, 1958, **10** (3), 153–156.—For the determination of electrode potentials, specifically for potentiometric titrations, the method employed involves the use of filter-paper strips impregnated with buffer soln. of standard pH, introduced in the cell circuit to obtain zero galvanometer deflection. The method is illustrated with antimony and glass electrodes. J. L. PROSSER

4399. **Performance of a wide-range high-frequency titration apparatus.** A. H. Johnson and A. Timnick (Kedzie Chem. Lab., Michigan State Univ., E. Lansing, U.S.A.). *Anal. Chem.*, 1958, **30** (8), 1324–1327.—The apparatus was modified to respond only to changes in the conductivity of the soln. by replacing the multi-turn coil by a single-turn loop. The instrument responds satisfactorily to aq. soln. of NaCl of concn. between 0·003 *M* and 5·0 *M*. Direct titration of 3 *N* HCl with 4 *N* NaOH has also been accomplished. K. A. PROCTOR

4400. **Electrometric titrations using two indicator electrodes. I. A theoretical interpretation of the "dead-stop end-point" method.** Sheau-Shya Kao and Kwang-Hsien Hsu (Dept. of Chem., Peking Univ.). *Acta Chim. Sinica*, 1958, **24** (1), 1–12.—The theory of the dead-stop end-point method is discussed. Equations are derived to express the ratio of current i/i_o, concn. of the soln., and steepness of the current change near the end-point as functions of the applied voltage, initial concn. of the soln., temp., electrode area, stirring rate and total resistance. Based on these equations, the theoretical titration curves and their slopes near the end-point for 2 reversible redox couples may be calculated. An applied voltage over several hundreds of mV is usually disadvantageous in the titration, but too small an applied voltage is inconvenient as a very sensitive galvanometer is required. The sensitivity of the titration at a given applied voltage is increased when a high resistance is inserted in the circuit.

II. Experimental verification of the "dead-stop" titration curves. Sheau-Shya Kao, Kwang-Hsien Hsu and T'sing-Chüan Tien. *Ibid.*, 1958, **24** (1), 12–18.—The theory of the dead-stop titrations developed in Part I has been verified in the titration of $Ce(SO_4)_2$ with Fe^{2+}. The titration curves obtained under various conditions and those calculated are given. The theoretical conclusions have been mainly confirmed, but there are several minor points of discrepancy between experimental and theoretical titration curves. The causes for these discrepancies are discussed. S. H. YUEN

4401. **Study of the behaviour of certain metals as micro-electrodes in amperometric titration.** T. K. Musina and O. A. Songina. *Uch. Zap. Alma-Atinsk. Gos. Ped. Inst.*, 1957, **8**, 174–185; *Ref. Zhur., Khim.*, 1958, Abstr. No. 39,320.—The use of gold, silver, copper, tungsten and tantalum as micro-electrodes for amperometric titration is studied. Electrodes of tungsten and tantalum were prepared as 8 × 1·5 mm and 5 × 1 mm plates, and of silver, copper and gold as wir of length 5 mm and diam. 1 mm. For all electrodes the studies were carried out under the following conditions—0·1 *M* H_2SO_4 (pH 1); acetic acid (pH 4); 1·75 *M* NH_4Cl - 0·02 *M* NaOH (pH 8); 0·025 *M* Na acetate - 0·02 *M* NaOH (pH 10); and 0·02 *M* NaOH (pH 12). A mercury electrode was used as comparison electrode ($E_o = +0{\cdot}017$ V *vs.* the hydrogen electrode). The behaviour of the micro-electrodes was studied both with cathodic and anodic polarisation. It is shown that copper and tantalum electrodes cannot be used for amperometric titration in either the cathodic or the anodic region; copper because of the high reactivity of the metal, and tantalum because of its inertness and easy passivation. Gold electrodes have a very high potential of liberation of O (+0·5 V in alkaline and from +1·0 to +1·2 V in acid soln.); gold is a very good material for electrodes with anodic polarisation. The tungsten electrode may be used for cathodic polarisation ($E_H = -0{\cdot}5$ V) but cannot be used for anodic polarisation. The silver electrode has a low potential of reduction of O in the anodic region (+0·4 V), but can be successfully employed for cathodic polarisation in certain processes ($E_H = -0{\cdot}4$ V at pH 4 and $-1{\cdot}2$ V at pH 10 to 12). C. D. KOPKIN

4402. **Improved NMR spectrometer.** J. M. Mays, H. R. Moore and R. G. Schulman (Bell Telephone Lab., Murray Hill, New Jersey). *Rev. Sci. Instrum.*, 1958, **29** (4), 300–302.—The instrument described

is an improved version of the Pound - Knight - Watkins nuclear magnetic resonance spectrometer in which frequency fluctuations are reduced by a factor of 5 to 10 at 30 Mc. It gives stable sensitive metering down to an r.f. level of 0·01 V across the sample coil and allows direct measurement of the derivative of χ', the real part of the susceptibility of the sample. G. SKIRROW

4403. **Analysis of gases at very low pressures by using the omegatron spectrometer.** J. S. Wagener and P. T. Marth (Kemet Co., Div. of Union Carbide Corp., Cleveland, Ohio). *J. Appl. Phys.*, 1957, **28** (9), 1027–1030.—An ion-resonance mass spectrometer is described which is capable of detecting and analysing gases up to mass number 44 at pressures as low as 10^{-10} mm. The omegatron, with its auxiliary vacuum equipment, has been applied to the analysis of gas evolved from materials used in high-vacuum work, to the analysis of residual gases, before and after the use of getters of the flash type, in television tubes, and to the investigation of gas reactions and dissociations. P. T. BEALE

4404. **A circulating pump for quantitative estimation of serial radio-isotope uptake *in vitro*.** D. R. Osgood, J. D. Boyd and A. S. Blum (Special Dental Res. Lab., Veterans Admin. Hosp., Coral Gables, Florida). *Intern. J. Appl. Radiation and Isotopes*, 1958, **3** (1), 43–44.—An apparatus is described and illustrated in which a radio-isotope in as little as 2·5 ml of soln. is passed through an immersion chamber for the specimen. Included in the circuit is a coil of tubing wound round a Geiger - Müller counter so that the radio-isotope concn. may be continuously recorded. G. J. HUNTER

4405. **Use of *iso*propyldiphenyl as solvent in liquid scintillators.** W. L. Buck and R. K. Swank (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Rev. Sci. Instrum.*, 1958, **29** (3), 252.—Liquid scintillating soln. with *iso*propyldiphenyl as solvent give light intensities comparable with those from the corresponding soln. in toluene. The greater density of atom electrons in *iso*propyldiphenyl gives it increased counting efficiency for gamma rays.
G. SKIRROW

4406. **Practical aspects of integral-sample liquid-scintillation counting.** J. D. Davidson and P. Feigelson (Dept. of Medicine and Biochem., College of Physicians and Surgeons, Columbia Univ., U.S.A.). *Intern. J. Radiation Isotopes*, 1957, **2** (1) 1–18.—The technique is of particular value in the assay of low-energy β-particles, and the counting of purines labelled with ^{14}C is specifically described. The use of the counting equipment and the selection of solvents and phosphors are discussed in detail.
G. J. HUNTER

4407. **Absolute assay and study of short-lived radionuclides by a recoil technique.** F. S. Rowland and R. L. Wolfgang (Dept. of Chem., Brookhaven Nat. Lab., Upton, L.I., N.Y.). *Rev. Sci. Instrum.*, 1958, **29** (3), 210–214.—The nuclear recoil of the product isotope (^6He) separates it from the target material and carries it into a carrier gas which passes into a counter. The data can be translated directly into absolute cross-sections without explicit knowledge of the recoil properties of the product.
G. SKIRROW

4408. **Application of thoria - iridium as the source of ionising electrons in mass spectrometry.** C. E. Melton (Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Rev. Sci. Instrum.*, 1958, **29** (3), 250.—Compared with tungsten filaments, thoria - iridium has the advantage of low operating and source temperatures and is resistant to corrosive gases.
G. SKIRROW

4409. **Solid-sample mass-spectrometer analyses of enriched stable isotopes.** J. R. Walton (Oak Ridge Nat. Lab., Oak Ridge, Tenn.). *U.S. Atomic Energy Comm.*, Rep. ORN-L2315, 1957, 10 pp.—Techniques, oven materials, ion sources, ions employed and other pertinent data are presented for mass-spectrometric analyses of enriched stable isotopes of 53 elements. CHEM. ABSTR.

4410. **Standardisation of mass spectra by means of total ion intensity.** A. Hood (Houston Res. Lab., Shell Oil Co., Tex., U.S.A.). *Anal. Chem.*, 1958, **30** (7), 1218–1220.—The use of this method in which the peak heights are summated overcomes the problem of sample vol. and instrument sensitivity in the analysis of petroleum oils and related compounds. The method has been applied to the correlation of mass spectra with molecular structure and to the analysis of lubricating-oil saturate fractions. K. A. PROCTOR

4411. **Rhenium as an electron emitter in mass spectrometry.** C. F. Robinson and A. G. Sharkey, jun. (Consolidated Electrodynamics Corp., Pasadena, Calif., U.S.A.). *Rev. Sci. Instrum.*, 1958, **29** (3), 250–251.—Replacement of the tungsten wire on a standard filament assembly for an analytical mass spectrometer with a rhenium wire gave improved performance owing to the absence of gas-sensitivity effects and formation of carbide on the emitter.
G. SKIRROW

4412. **Magnetic mass spectrometer.** L. Furman and V. Vrščaj ("J. Stefan" Inst., Ljubljana, Yugoslavia). *Rep. "J. Stefan" Inst., Ljubljana*, 1957, **4**, 109–115 (in English).—The construction, operation and performance of an instrument built at the Institute is described. A dual sample inlet system enables two samples to be compared and a separate inlet system is used for gases. Ionisation of gaseous samples is achieved by means of an electron beam emitted from a tungsten filament and collimated magnetically. This beam is stabilised within $\pm$ 2%. The ion-accelerating voltage is continuously variable from 0 to 2 kV with a ripple of < 50 mV. The ion-separating magnet has a 1·4-cm gap and a 60° sector angle, giving a radius of curvature of 15 cm. The flux density in the gap is variable up to 7000 gauss. Ions are identified by the accelerating voltage and the strength of the separating field, and quantitatively determined by the collector current which is fed through amplifiers into a recorder and an oscillograph. The mass range covered is 1 to 400 atomic mass units. The resolving power (*i.e.*, the highest mass number at which a difference of 1 mass unit can be resolved) is 350 (theoretical, 400). The sensitivity (*i.e.*, the minimum relative quantity of any component detectable) is 3×10^{-5}. The accuracy of the instrument has been proved by recording the spectrum of Xe. The relative isotopic abundances are compared with their standard values. The mass spectrum of UF_6 has also been recorded.
G. BURGER

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic.	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
constant	const.
corrected	(corr.)
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_λ^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_{F}
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{3+}, Fe^{2+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

is an improved version of the Pound - Knight - Watkins nuclear magnetic resonance spectrometer in which frequency fluctuations are reduced by a factor of 5 to 10 at 30 Mc. It gives stable sensitive metering down to an r.f. level of 0·01 V across the sample coil and allows direct measurement of the derivative of χ', the real part of the susceptibility of the sample. G. SKIRROW

4403. **Analysis of gases at very low pressures by using the omegatron spectrometer.** J. S. Wagener and P. T. Marth (Kemet Co., Div. of Union Carbide Corp., Cleveland, Ohio). *J. Appl. Phys.*, 1957, **28** (9), 1027–1030.—An ion-resonance mass spectrometer is described which is capable of detecting and analysing gases up to mass number 44 at pressures as low as 10^{-10} mm. The omegatron, with its auxiliary vacuum equipment, has been applied to the analysis of gas evolved from materials used in high-vacuum work, to the analysis of residual gases, before and after the use of getters of the flash type, in television tubes, and to the investigation of gas reactions and dissociations. P. T. BEALL

4404. **A circulating pump for quantitative estimation of serial radio-isotope uptake *in vitro*.** D. R. Osgood, J. D. Boyd and A. S. Blum (Special Dental Res. Lab., Veterans Admin. Hosp., Coral Gables, Florida). *Intern. J. Appl. Radiation and Isotopes*, 1958, **3** (1), 43–44.—An apparatus is described and illustrated in which a radio-isotope in as little as 2·5 ml. of soln. is passed through an immersion chamber for the specimen. Included in the circuit is a coil of tubing wound round a Geiger - Müller counter so that the radio-isotope concn. may be continuously recorded. G. J. HUNTER

4405. **Use of *iso*propyldiphenyl as solvent in liquid scintillators.** W. L. Buck and R. K. Swank (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Rev. Sci. Instrum.*, 1958, **29** (3), 252.—Liquid scintillating soln. with *iso*propyldiphenyl as solvent give light intensities comparable with those from the corresponding soln. in toluene. The greater density of atom electrons in *iso*propyldiphenyl gives it increased counting efficiency for gamma rays.
G. SKIRROW

4406. **Practical aspects of integral-sample liquid-scintillation counting.** J. D. Davidson and P. Feigelson (Dept. of Medicine and Biochem., College of Physicians and Surgeons, Columbia Univ., U.S.A.). *Intern. J. Radiation Isotopes*, 1957, **2** (1), 1–18.—The technique is of particular value in the assay of low-energy β-particles, and the counting of purines labelled with ^{15}N is specifically described. The use of the counting equipment and the selection of solvents and phosphors are discussed in detail.
G. J. HUNTER

4407. **Absolute assay and study of short-lived radionuclides by a recoil technique.** F. S. Rowland and R. L. Wolfgang (Dept. of Chem., Brookhaven Nat. Lab., Upton, L.I., N.Y.). *Rev. Sci. Instrum.*, 1958, **29** (3), 210–214.—The nuclear recoil of the product isotope (^{6}He) separates it from the target material and carries it into a carrier gas which passes into a counter. The data can be translated directly into absolute cross-sections without explicit knowledge of the recoil properties of the product.
G. SKIRROW

4408. **Application of thoria - iridium as the source of ionising electrons in mass spectrometry.** C. F. Melton (Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Rev. Sci. Instrum.*, 1958, **29** (3), 250.—Compared with tungsten filaments, thoria - iridium has the advantage of low operating and source temperatures and is resistant to corrosive gases.
G. SKIRROW

4409. **Solid-sample mass-spectrometer analyses of enriched stable isotopes.** J. R. Walton (Oak Ridge Nat. Lab., Oak Ridge, Tenn.). *U.S. Atomic Energy Comm.*, Rep. ORNL-2315, 1957, 10 pp.—Techniques, oven materials, ion sources, ions employed and other pertinent data are presented for mass-spectrometric analyses of enriched stable isotopes of 53 elements. CHEM. ABSTR.

4410. **Standardisation of mass spectra by means of total ion intensity.** A. Hood (Houston Res. Lab., Shell Oil Co., Tex., U.S.A.). *Anal. Chem.*, 1958, **30** (7), 1218–1220.—The use of this method in which the peak heights are summated overcomes the problem of sample vol. and instrument sensitivity in the analysis of petroleum oils and related compounds. The method has been applied to the correlation of mass spectra with molecular structure and to the analysis of lubricating oil saturate fractions. K. A. PROCTOR

4411. **Rhenium as an electron emitter in mass spectrometry.** C. F. Robinson and A. G. Sharkey jun. (Consolidated Electrodynamics Corp., Pasadena, Calif., U.S.A.). *Rev. Sci. Instrum.*, 1958, **29** (3), 250–251.—Replacement of the tungsten wire on a standard filament assembly for an analytical mass spectrometer with a rhenium wire gave improved performance owing to the absence of gas-sensitivity effects and formation of carbide on the emitter.
G. SKIRROW

4412. **Magnetic mass spectrometer.** L. Furman and V. Vrščaj ("J. Stefan" Inst., Ljubljana, Yugoslavia). *Rep. "J. Stefan" Inst., Ljubljana*, 1957, **4**, 109–115 (in English).—The construction, operation and performance of an instrument built at the Institute is described. A dual sample inlet system enables two samples to be compared and a separate inlet system is used for gases. Ionisation of gaseous samples is achieved by means of an electron beam emitted from a tungsten filament and collimated magnetically. This beam is stabilised within ± 2%. The ion-accelerating voltage is continuously variable from 0 to 2 kV with a ripple of < 50 mV. The ion-separating magnet has a 1·4-cm gap and a 60° sector angle, giving a radius of curvature of 15 cm. The flux density in the gap is variable up to 7000 gauss. Ions are identified by the accelerating voltage and the strength of the separating field, and quantitatively determined by the collector current which is fed through amplifiers into a recorder and an oscillograph. The mass range covered is 1 to 400 atomic mass units. The resolving power (*i.e.*, the highest mass number at which a difference of 1 mass unit can be resolved) is 350 (theoretical, 400). The sensitivity (*i.e.*, the minimum relative quantity of any component detectable) is 3×10^{-5}. The accuracy of the instrument has been proved by recording the spectrum of Xe. The relative isotopic abundances are compared with their standard values. The mass spectrum of UF_6 has also been recorded.
G. BURGER

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
constant	const.
corrected	(corr.)
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_λ^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_F
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{2+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

Volume 5. No. 12, Abstracts 3961-4412 December, 1958

ANALYTICAL ABSTRACTS

A PUBLICATION OF
THE SOCIETY FOR ANALYTICAL CHEMISTRY

EDITORIAL COMMITTEE

Chairman: R. C. Chirnside

Members: B. S. Cooper, B. A. Ellis, C. H. R. Gentry, C. A. Johnson, I. MacIntyre, B. J. Walby, W. A. Waygood and the President and Honorary Officers

President of the Society: J. H. Hamence

Hon. Secretary of the Society: R. E. Stuckey

Hon. Assistant Secretary of the Society: S. A. Price

Hon. Treasurer of the Society: A. J. Amos

Editor: Norman Evers, B.Sc., Ph.D., F.R.I.C.

Assistant Editor: Mrs. H. I. Fisk, B.Sc.

CONTENTS

	Abstract
General Analytical Chemistry	3961
Inorganic Analysis	3986
Organic Analysis	4153
Biochemistry	
Blood, Bile, Urine, etc.	4228
Drugs	4272
Food	4305
Sanitation	4324
Agriculture and Plant Biochemistry	4332
General Technique and Laboratory Apparatus	
General	4353
Optical	4368
Thermal	4378
Electrical	4380

Printed and Published for the Society for Analytical Chemistry by W. Heffer & Sons Ltd., Cambridge, England
Communications to be addressed to the Editor, Norman Evers, 14, Belgrave Square, London, S.W.1.
Enquiries about advertisements should be addressed to Walter Judd Ltd., 47, Gresham Street, London, E.C.2.
Entered as Second Class at New York, U.S.A., Post Office